THE

PHYSICAL SOCIETY

OF

LONDON.

PROCEEDINGS.

VOLUME XVI.—PART V.

MAY 1899.

LONDON:
TAYLOR AND FRANCIS, RED LION COURT, FLEET STREET.
1899.

PHYSICAL SOCIETY OF LONDON.

1899–1900.

OFFICERS AND COUNCIL.

President.

PROF. OLIVER J. LODGE, D.Sc., LL.D., F.R.S.

Vice-Presidents

WHO HAVE FILLED THE OFFICE OF PRESIDENT.

DR. J. H. GLADSTONE, F.R.S.
PROF. G. C. FOSTER, F.R.S.
PROF. W. G. ADAMS, M.A., F.R.S.
THE LORD KELVIN, D.C.L., LL.D., F.R.S.
PROF. R. B. CLIFTON, M.A., F.R.S.
PROF. A. W. REINOLD, M.A., F.R.S.
PROF. W. E. AYRTON, F.R.S.
PROF. G. F. FITZGERALD, M.A., F.R.S.
PROF. A. W. RÜCKER, M.A., D.Sc., Sec. R.S.
CAPT. W. DE W. ABNEY, R.E., C.B., D.C.L., F.R.S.
SHELFORD BIDWELL, M.A., LL.B., F.R.S.

Vice-Presidents.

T. H. BLAKESLEY, M.A.
C. VERNON BOYS, F.R.S.
G. GRIFFITH, M.A.
PROF. J. PERRY, D.Sc., F.R.S.

Secretaries.

H. M. ELDER, M.A.
50 *City Road, E.C.*

W. WATSON, B.Sc.
7 *Upper Cheyne Row, Chelsea, S.W.*

Foreign Secretary.

PROF. S. P. THOMPSON, D.Sc., F.R.S.

Treasurer.

DR. E. ATKINSON.
Portesbery Hill, Camberley, Surrey.

Librarian.

W. WATSON, B.Sc.
Royal College of Science, South Kensington.

Other Members of Council.

PROF. H. E. ARMSTRONG, D.Sc., F.R.S.
WALTER BAILY, M.A.
R. E. CROMPTON.
PROF. J. D. EVERETT, D.C.L., F.R.S.
PROF. A. GRAY, LL.D., F.R.S.
E. H. GRIFFITHS, M.A., F.R.S.
PROF. J. VIRIAMU JONES, M.A., F.R.S.
S. LUPTON, M.A.
PROF. G. M. MINCHIN, M.A., F.R.S.
J. WALKER, M.A.

XXX. *On the Propagation of Damped Electrical Oscillations along Parallel Wires. By* Prof. W. B. MORTON, *M.A.*[*]

IN a paper published in the 'Proceedings' of the Physical Society (*ante*, p. 219), Dr. E. H. Barton has compared the attenuation of electrical waves in their passage along parallel wires, as experimentally determined by him, with the formula given by Mr. Heaviside in his theory of long waves. The results show a large discrepancy between the theory and the experiments, the observed value of the attenuation constant being about twice too large. Dr. Barton discusses several possible causes of error and finds them inadequate, and suggests that the reason of the difference may lie either in (1) the nearness of the wires to one another, or (2) in the damping of the wave-train propagated by the oscillator. To these may be added (3) the consideration that the formulæ used were deduced by Mr. Heaviside from the discussion of his "distortionless circuit," in which the matter is simplified by supposing sufficient leakage to counteract the distortion produced by the resistance of the leads, whereas in Dr. Barton's circuit the leakage was negligible.

It is probable that the nearness of the wires has an appreciable effect on the phenomenon. The discrepancy would be diminished if the actual resistance of the wires was greater than that calculated by Dr. Barton from Lord Rayleigh's high-frequency formula. Now the effect of the neighbourhood of two wires carrying rapidly oscillating currents in opposite directions is to make the currents concentrate towards the inner sides of the wires[†]; and this would cause an increase in the effective resistance.

I have examined the effects of (2) and (3), viz. of the damping and the want of balance in the constants of the circuit. The investigation is perhaps of some interest owing to the fact that these elements are always present in the ordinary experimental conditions; although, as will be seen, we are led to the conclusion that in all actual cases their influence on the phenomena is of quite negligible order. The method is the same as that used by Mr. Heaviside.

---

[*] Read November 11, 1898.

[†] *Cf.* J. J. Thomson, 'Recent Researches,' p. 511.

General Theory.—Let the inductance of the circuit be L, its capacity S, its resistance (of double wires) R, and its leakage-conductance K, all per unit length. An important part is played by the ratios $\frac{\mathrm{R}}{\mathrm{L}}$ and $\frac{\mathrm{K}}{\mathrm{S}}$; we shall call these ρ and σ. When ρ and σ are equal we have the "distortionless" circuit above referred to.

Now if V be the difference of potential between the wires and C the current in the positive wire, we have the equations

$$-\frac{d\mathrm{V}}{dz}=\left(\mathrm{R}+\mathrm{L}\frac{d}{dt}\right)\mathrm{C}, \quad \ldots \ldots \ldots \quad (1)$$

$$-\frac{d\mathrm{C}}{dz}=\left(\mathrm{K}+\mathrm{S}\frac{d}{dt}\right)\mathrm{V}; \quad \ldots \ldots \ldots \quad (2)$$

giving

$$\frac{d^2\mathrm{V}}{dz^2}=\left(\mathrm{R}+\mathrm{L}\frac{d}{dt}\right)\left(\mathrm{K}+\mathrm{S}\frac{d}{dt}\right)\mathrm{V}$$

$$=\frac{1}{v^2}\left(\rho+\frac{d}{dt}\right)\left(\sigma+\frac{d}{dt}\right)\mathrm{V}, \quad \ldots \ldots \quad (3)$$

since $\mathrm{LS}v^2=1$, where v is the velocity of radiation.

To simplify the algebra we shall work first with $\mathrm{V}=\mathrm{V}_0e^{-mz+nt}$, which can be made to represent damped periodic vibrations by giving complex values to m and n.

The equation (3) now becomes

$$m^2v^2=(\rho+n)(\sigma+n); \quad \ldots \ldots \quad (4)$$

and the connexion between C and V is given by (1), viz.

$$\mathrm{C}=\frac{m\mathrm{V}}{\mathrm{R}+\mathrm{L}n}. \quad \ldots \ldots \ldots \quad (5)$$

To find the effect of a pure resistance R′ between the ends of the wires, as in Dr. Barton's experiments, put V_1, V_2, C_1, C_2 for the potentials and currents in the incident and reflected waves respectively. Then we have

$$\mathrm{C}_1=\frac{m\mathrm{V}_1}{\mathrm{R}+\mathrm{L}n}, \quad \mathrm{C}_2=\frac{-m\mathrm{V}_2}{\mathrm{R}+\mathrm{L}n};$$

also the total potential-difference V_1+V_2 is connected with total current C_1+C_2 through resistance R′ by Ohm's law,

$$V_1+V_2=R'(C_1+C_2).$$

These equations give for the reflexion factor

$$\frac{V_2}{V_1}=-\frac{R+Ln-mR'}{R+Ln+mR'}. \quad . \quad . \quad . \quad . \qquad (6)$$

If the circuit be distortionless and $R'=Lv$, then, as Mr. Heaviside showed, the absorption of the waves by the terminal resistance will be complete. We may regard this as the critical resistance for the circuit, and we shall express R′ in terms of it by putting $R'=xLv$. We then have

$$\frac{V_2}{V_1}=-\frac{\rho+n-mvx}{\rho+n+mvx}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

Damped Wave-Train.—To pass to the case of a damped train transmitted from the origin in the positive direction of z we put

$$m=-\beta+i\alpha, \qquad n=-q+ip.$$

The difference of potential between the wires at any point after the head of the wave-train has reached this point is then represented by an expression of the form

$$V_0e^{\beta z-qt}\sin(pt-\alpha z).$$

The velocity of propagation is $\frac{p}{\alpha}$, the frequency $\frac{p}{2\pi}$, the logarithmic decrement $\frac{2\pi q}{p}$. If the waves suffered no attenuation in their passage along the leads we should have

$$\beta z-qt=0 \text{ when } z=\frac{pt}{\alpha}, \text{ i. e. } \beta=\frac{q\alpha}{p}.$$

In general, it is plain that $\left(\frac{q\alpha}{p}-\beta\right)$ measures the attenuation.

Inserting the complex variables in equation (4) we have

$$v^2(\beta-i\alpha)^2=(\rho-q+ip)(\sigma-q+ip);$$

$$\therefore \quad v^2(\beta^2-\alpha^2)=q^2-p^2-q(\rho+\sigma)+\rho\sigma; \quad . \quad . \quad . \quad . \qquad (8)$$

and

$$2v^2\alpha\beta=p(2q-\rho-\sigma); \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

whence

$$v^2(\beta^2+\alpha^2)=\sqrt{\{p^2+(q-\rho)^2\}\{p^2+(q-\sigma)^2\}}. \quad . \qquad (10)$$

Velocity of Propagation and Attenuation.—In actual cases ρ and σ are small compared with p. If the damping is considerable, q may be comparable with p. Accordingly we expand the right-hand side of (10) in ascending powers of ρ and σ and solve for $v\alpha$ and $v\beta$. As far as terms of the third order in ρ and σ we find

$$v^2\alpha = p + \frac{p(\rho-\sigma)^2}{8(p^2+q^2)} + \frac{pq(\rho+\sigma)(\rho-\sigma)^2}{8(p^2+q^2)^2} + \dots, \quad . \quad (11)$$

$$v\beta = q - \tfrac{1}{2}(\rho+\sigma) - \frac{q(\rho-\sigma)^2}{8(p^2+q^2)} + \frac{(p^2-q^2)(\rho+\sigma)(\rho-\sigma)^2}{16(p^2+q^2)^2} + \dots . \quad (12)$$

Hence the *velocity of propagation*

$$= \frac{p}{\alpha} = v\left[1 - \frac{(\rho-\sigma)^2}{8(p^2+q^2)} - \frac{q(\rho+\sigma)(\rho-\sigma)^2}{8(p^2+q^2)^2} - \dots\right], \quad . \quad (13)$$

and the *attenuation*

$$= \frac{q\alpha}{p} - \beta = \frac{1}{v}\left[\frac{\rho+\sigma}{2} + \frac{q(\rho-\sigma)^2}{4(p^2+q^2)} + \frac{(3q^2-p^2)(\rho+\sigma)(\rho-\sigma)^2}{16(p^2+q^2)^2} + \right]. \quad ($$

If $\rho=\sigma$, there is no distortion, the velocity of propagation is v, and the attenuation is $\frac{\mathrm{R}}{\mathrm{L}v}$ or $\frac{\mathrm{K}}{\mathrm{S}v}$ for all frequencies; and the damping has no effect on these quantities.

We have an interesting particular case when $\rho=\sigma=q$. Then $\beta=0$, and the state of affairs is given by

$$\mathrm{V} = \mathrm{V}_0 e^{-qt} \sin\left(pt - \frac{z}{v}\right).$$

Here the damping and the attenuation are balanced, so that the wave-train in the wires is at any instant *purely* simple harmonic throughout.

Numerical Values.—To obtain an estimate of the importance of the small terms of (13) and (14) I shall take the numbers given by Dr. Barton in his last paper (*loc. cit.*). Judging from his diagram (fig. 2) in that paper, the amplitude of the second positive maximum of the wave-train is about half that of the first. This would give

$$e^{\frac{2\pi q}{p}} = 2 \quad \text{or} \quad q = \frac{p \log_e 2}{2\pi}.$$

We have roughly

$$p=2\pi\times 35\times 10^6=22\times 10^7, \qquad q=24\times 10^6,$$

$$\mathrm{R}=69{\cdot}5\times 10^5, \qquad \mathrm{L}=19;$$

$$\therefore\quad \rho=37\times 10^4, \quad \text{and} \quad \sigma=0.$$

These values give for the velocity of propagation

$$v\{1-{\cdot}00000035\},$$

and for the attenuation

$$\frac{\mathrm{R}}{2\mathrm{L}v}\{1+{\cdot}000091\},$$

so that the corrections are quite negligible. We see from the expressions (13), (14) that the damping q only affects the value of the small terms introduced by the inequality of ρ and σ.

Effect of a Terminal Resistance.—To find the effect on the incident waves of a resistance (without inductance) inserted between the ends of the wires, we put in the complex values in the expression (7) for the reflexion-factor. We then get

$$\frac{\mathrm{V}_2}{\mathrm{V}_1}=\frac{(\rho-q+v\beta x)+i(p-v\alpha x)}{(-\rho+q+v\beta x)-i(p+v\alpha x)}$$
$$=f+ig, \text{ say.}$$

Therefore to an incident wave e^{ipt} corresponds a reflected wave $(f+ig)e^{ipt}$; or, taking real parts, with incident $\cos pt$ we have reflected

$$f\cos pt-g\sin pt=\sqrt{f^2+g^2}\cos(pt+\theta),$$

where

$$\tan\theta=\frac{g}{f};$$

so that the change of amplitude is accompanied by a change of phase.

The values come out

$$f^2+g^2=\frac{(\rho-q+v\beta x)^2+(p-v\alpha x)^2}{(-\rho+q+v\beta x)^2+(p+v\alpha x)^2} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$=\frac{x^2v^2(\alpha^2+\beta^2)-2xv\{\beta(q-\rho)+\alpha p\}+(q-\rho)^2+p^2}{x^2v^2(\alpha^2+\beta^2)+2xv\{\beta(q-\rho)+\alpha p\}+(q-\rho)^2+p^2}, \quad (16)$$

$$\frac{g}{f}=\frac{2xv\{\beta p-\alpha(q-\rho)\}}{x^2v^2(\alpha^2+\beta^2)-(q-\rho)^2-p^2}. \quad \text{(17)}$$

In order that there should be complete absorption of the incident waves it is necessary that the two squares in the numerator of (15) should vanish separately. This requires

$$\frac{v\alpha}{p}=\frac{v\beta}{q-\rho}=\lambda, \text{ say.}$$

If we substitute $v\alpha=p\lambda$ and $v\beta=(q-\rho)\lambda$ in equations (8) and (9), and eliminate λ by division, we find the condition reduces to

$$(\rho-\sigma)\{(q-\rho)^2+p^2\}=0, \qquad \therefore\ \rho=\sigma.$$

Therefore complete absorption is only attainable in the distortionless case. In general we can only reduce the reflected amplitude to a minimum.

We can write (16) and (17) in the forms

$$f^2+g^2=\frac{ax^2-2hx+b}{ax^2+2hx+b}, \quad \text{(18)}$$

$$\tan\theta=\frac{g}{f}=\frac{2x\sqrt{ab-h^2}}{ax^2-b}. \quad \text{(19)}$$

From (18) we see that to any value of reflected amplitude correspond two values of the terminal resistance, say x_1, x_2. We can show that the corresponding phase-differences θ_1, θ_2 are supplementary.

For from (18) we have

$$x_1x_2=\frac{b}{a};$$

$$\therefore\ \tan\theta_1+\tan\theta_2=2\sqrt{ab-h^2}\left[\frac{x_1}{ax_1^2-b}+\frac{x_2}{ax_2^2-b}\right]$$

$$=2\sqrt{ab-h^2}\,\frac{(x_1+x_2)(ax_1x_2-b)}{(ax_1^2-b)(ax_2^2-b)}=0.$$

The minimum reflected amplitude is got when

$$x_1=x_2=\sqrt{\frac{b}{a}}.$$

The reflexion-factor is then $\frac{\sqrt{ab}-h}{\sqrt{ab}+h}$, and the phase-difference is $\frac{\pi}{2}$. When $x=0$ we have complete reflexion with unaltered phase; with $x=\infty$, or the circuit open, we have complete reflexion with reversed phase. The simultaneous alteration of amplitude and phase-difference brings it about that we appear to pass continuously from amplitude $+1$ ($x=0$) to amplitude -1 ($x=\infty$) without passing through amplitude zero. This apparent anomaly was pointed out to me by Dr. Barton. Putting in the values of a, b, h, and substituting for $v\alpha$ and $v\beta$ approximate values from (11), (12), we find that the minimum value of the reflexion-factor $\sqrt{f^2+g^2}$ is

$$\frac{p(\rho-\sigma)}{4(p^2+q^2)},$$

and that the corresponding value of x is

$$1-\frac{q(\rho-\sigma)}{2(p^2+q^2)},$$

neglecting higher terms in $\rho\sigma$.

Numerical Values.—Again using Dr. Barton's numbers we get for the minimum reflexion-factor the value ·0004, and for the corresponding terminal resistance $Lv(1+{\cdot}00009)$. If, therefore, the terminal resistance be adjusted until the reflected wave is a minimum, we may, without sensible error, take this resistance to be Lv, and ignore the reflected train altogether.

Queen's College, Belfast,
13th October, 1898.

DISCUSSION.

Mr. OLIVER HEAVISIDE (communicated).—The connexion between the case investigated by Mr. Morton of a wave-train arising from a damped source and the standard case of an undamped source may be concisely exhibited thus. Using the notation of 'Electromagnetic Theory,' vol. i. p. 452, we have

$$V=\epsilon^{-qx}V_0, \quad \text{. . . . .} \quad (1)$$

where

$$q=(R+Lp)^{\frac{1}{2}}(K+Sp)^{\frac{1}{2}}, \quad \text{. . . . . .} \quad (2)$$

to express the wave-train V due to V_0 at $x=0$. When V_0 is simply periodic, say $=e \sin nt$, then $p=ni$ reduces q to $P+Qi$, given by

$$\text{P or Q} = (\tfrac{1}{2})^{\frac{1}{2}} \{ (R^2+L^2n^2)^{\frac{1}{2}} (K^2+S^2n^2)^{\frac{1}{2}} \pm (RK-LSn^2) \}^{\frac{1}{2}},$$

$$= (\tfrac{1}{2})^{\frac{1}{2}} \frac{n}{v} \left\{ \left(1+\frac{R^2}{L^2n^2}\right)^{\frac{1}{2}} \left(1+\frac{K^2}{S^2n^2}\right)^{\frac{1}{2}} \pm \left(\frac{RK}{LSn^2}-1\right) \right\}^{\frac{1}{2}}, \quad . \quad (3)$$

so that the solution is

$$V = e\epsilon^{-Px} \sin (nt-Qx). \quad . \quad . \quad . \quad . \quad (4)$$

Now if V_0 be damped, say $=e_0\epsilon^{-at} \sin nt$, the effect of shifting ϵ^{-at} to the left is to change p to $p-a$ in the operator ϵ^{-qx}, that is, in q. This is the same as changing R to R_0 and K to K_0, given by

$$R_0 = R - La, \qquad K_0 = K - La, \quad . \quad . \quad . \quad . \quad (5)$$

so that the wave-train is

$$V = e_0 \, \epsilon^{-at} \, \epsilon^{-P'x} \sin (nt-Q'x), \quad . \quad . \quad . \quad . \quad (6)$$

where P′ and Q′ are the same as P and Q with R_0 and K_0 instead of R and K. Of course R and K are positive, and q is in the first quadrant, but the new R_0 and K_0 may be positive or negative, and q may be in the second quadrant.

Practically, under the circumstances of the experiments,

$$Q' = \frac{n}{v} \quad \text{and} \quad P' = \frac{1}{2v}\left(\frac{R}{L}+\frac{K}{S}\right) - \frac{a}{v}, \quad . \quad . \quad . \quad (7)$$

where K is negligible, and

$$V = e_0 \, \epsilon^{-at} \, \epsilon^{ax/v} \, \epsilon^{-Rx/2Lv} \sin (nt - nx/v). \quad . \quad . \quad . \quad (8)$$

As regards the cause of the attenuating coefficient $R/2Lv$ coming out by Dr. Barton's calculations from his experiments twice as great as when R is calculated by Lord Rayleigh's formula, I think it must be because the real circumstances do not correspond closely enough to those in the ideal theory. The external resistance, of unknown amount, is ignored, for one thing. Then again, it is not to be certainly expected that the formula in question is true for millions of vibrations per second. We can conclude from the experiments, though, that it furnishes an approximation to the real resistance.

But, even if it were rigorously true, the circumstances implied in it are not those in the experiments. The magnetic vibrations to which the wires are subjected are not long continued and undamped, as assumed in the formula. When a wave-train passes any point on a wire, its surface is subjected to an impulsive vibration lasting only a very minute fraction of a second, a vibration, moreover, which is very rapidly damped. So there is no definite resistance, and the resistance is greater than according to Lord Rayleigh's formula.

Perhaps, also, the terminal reflexions involved in Dr. Barton's calculations may introduce error.

XXXI. *Properties of Liquid Mixtures.*—Part III.*

Partially Miscible Liquids. By R. A. Lehfeldt, *D.Sc.*†

The phenomena of complete mixture between two liquids, about which so little systematic knowledge is yet in existence, are connected with the phenomena of ordinary solution by an intermediate stage, that in which two liquids dissolve one another to a limited extent only. The study of such couples seems a promising field of investigation, on account of the intermediate position they occupy; it seems to offer the chance of extending some of the laws arrived at with regard to simple solution to the more complicated cases. I have therefore attempted to get some information on the equilibrium between incomplete mixtures and the vapour over them, and especially at the "critical point," *i. e.*, the point at which incomplete miscibility passes over into complete. A recent short paper by Ostwald ‡ draws attention to the importance of that point in the theory of mixtures.

Choice of Liquids.

The first point is to obtain suitable pairs of liquids for experiment. In order to study the properties of the critical point with ordinary vapour-pressure apparatus, it is necessary that the pressure at the critical point should be below one atmosphere, and that limits very much the choice of liquids. As a rule, two liquids either mix completely cold, or if they do not do that, raising to the boiling-point does not suffice to make them mix; two or three cases are all that I have been able to find in which the point of complete mixture can be arrived at by boiling, and consequently corresponds to a vapour-pressure below the atmospheric. Many other pairs of incompletely miscible liquids have been studied by Alexejew and others, but to arrive at their critical points it was necessary to raise them to a high temperature in sealed tubes. A recent paper by Victor Rothmund * contains new observations on the relation between concentration and temperature, including the concentration and temperature of the critical point, made by Alexejew's method. That paper contains a long account of previous work on the subject, which makes it the less necessary for me to go over the same ground. I will therefore mention only what has been done on vapour-pressures, as Rothmund does not touch on that side of the subject, merely adding two remarks to his paper. First, it does not seem to have been noticed that normal organic liquids always mix completely: I hoped to have found a normal pair to study first, in order to avoid the complication due to the abnormality supposed to be molecular aggregation in the liquid; I have not succeeded in finding such a pair. All the incompletely miscible pairs of liquids so far noted include water, methyl alcohol, or a low fatty acid as one member. To those with accessible critical points mentioned by Rothmund, I have only one pair to add, viz., ethylene dibromide and formic acid; these mix on boiling and separate into two layers when cold. I have not yet gone further with this couple; the vapour-pressure observations below refer to the well-known cases of phenol and water, aniline and water.

---

* Part I. Phil. Mag. (5) xl. p. 398; Part II. Phil. Mag. (5) xlvi. p. 46; reprinted, Proc. Phys. Soc. xvi. p. 83.

† Read November 25, 1898.

‡ Wied. *Ann.* lxiii. p. 336 (1897).

An account of previous experiments on the vapour-pressure of incompletely miscible liquids will indeed not take up much space, since, so far as I know, there is only one to record,

---

* *Zeitschr. f. phys. Chem.* xxvi. p. 433 (1898).

viz., Konowalow's [*] measurements on isobutyl alcohol-water mixtures. His observations (made by a static method) give some points on the vapour-pressure curve up to 100° for (1) pure isobutyl alcohol (100 $^0/_0$) ; (2) mixtures containing 94·05 $^0/_0$ and 6·17 $^0/_0$, both clear; (3) an undetermined mixture which separated into two layers. He unfortunately did not measure the solubility of the alcohol in water, or water in the alcohol, at any of the temperatures for which vapour-pressure observations are recorded, so those data have to be supplied from Alexejew's results [†]. Konowalow, in the second part [‡] of his paper, proceeds to show that the possible forms of curve showing vapour-pressure against concentration (temperature constant) are two : (i.) the flat part of the curve bounded by a rising portion at one end and a falling portion at the other ; (ii.) the flat part bounded by a falling portion at each end. Isobutyl alcohol-water mixtures give a curve of the latter kind.

Isobutyl alcohol and water, however, possess a critical point at about 130°, *i. e.*, much above the boiling-point of either. I therefore decided to study first mixtures of phenol and water, which become homogeneous in any proportions below 70°.

The phenol was a commercial "pure" specimen ; to purify it further, it was placed in a distillation-flask and melted ; then air was drawn through it for about half an hour, whilst its temperature was kept at about 160° to 170°, in order to dry it. It was then distilled, and by far the larger part came over between 178° and 180°. The fraction collected between 179°·5 and 180° (about half the mass) was used in the experiments. To make up mixtures, the process always adopted was to warm the stoppered bottle containing the phenol to just above the melting-point, and pour the required amount into a weighing-flask. It was found that the moisture absorbed from the air during the process was quite inappreciable. The phenol, kept day after day at 40° to 50° ready for use, slowly turned pink, showing the presence of rosolic acid ; but a comparative colour-observation showed that the amount of impurity was probably not more than 1/10,000. When it was necessary to estimate phenol in a mixture, that was done by the method of Koppeschaar, tribromphenol being formed and the excess of bromine replaced by iodine and titrated with thiosulphate. The method gave quite satisfactory results.

---

[*] Wied. *Ann.* xiv. p. 43.

[†] Wied. *Ann.* xxviii. p. 315.

[‡] Wied. *Ann.* xiv. p. 222.

Experimental Methods used.

The measurements on phenol-mixtures gave results contrary to my expectations, so that I became suspicious of the experimental methods. In the end I made use of four different kinds of apparatus, but found that they gave results in practical agreement, so that it became chiefly a question of convenience to decide between them.

The first method tried was the "dynamic," carried out with the same apparatus as described in Part II. It required no modification, except the use of a new thermometer, since the old one did not go above 60°. The new thermometer was a longer one, graduated in $\frac{1}{5}$ from 0° to 100° (by C. E. Müller, No. 8). Its corrections were obtained in two ways: first by comparison with a standard (Reichsanstalt, 7347) at certain fixed temperatures, viz., the boiling-points of methyl acetate (57°), methyl alcohol (65°), and ethyl alcohol (78°); secondly, by measurements of the vapour-pressures of water under the same conditions as in the actual experiments; in these conditions part of the stem was exposed.

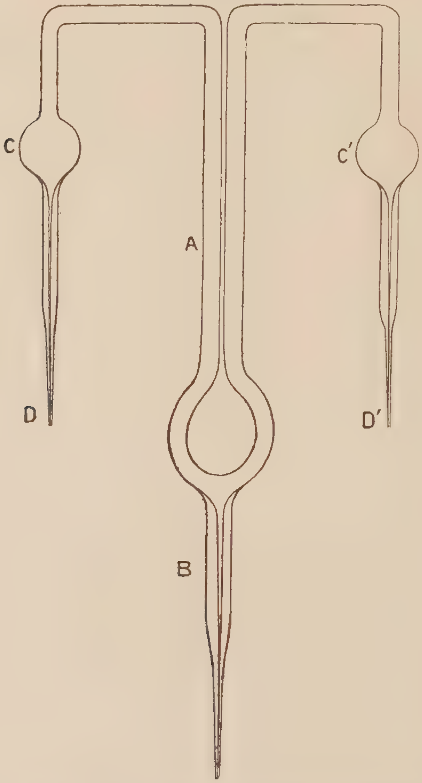
To use the apparatus the required mixture was weighed out from melted phenol and distilled water, then warmed up in the weighing-bottle until it became homogeneous, and poured into the tube of the vapour-pressure apparatus. The apparatus works satisfactorily except for mixtures on a very steep part of the curve of vapour-pressure (p) over concentration (z); when dp/dz is great, the change of composition of the liquid, due to the evaporation, becomes disproportionately important, and the static method is to be preferred; in the case of phenol mixtures, however, that only affects a small part of the range —mixtures with 90 per cent. or more of phenol.

The anomalous result that made me at first doubtful of the accuracy of the method was that the addition of up to 60 or

70 per cent. of phenol to water made practically no difference to the vapour-pressure of the water. To check this, I made one or two experiments by the static method, in a barometer-tube surrounded by an alcohol-vapour jacket of the usual pattern. They were not carried out with any attempt at accuracy, but sufficed to show that the previous observations could not be far wrong. The problem then was to determine the small difference in pressure between water and the phenol-water mixtures, and as for that purpose a differential gauge is obviously more appropriate, I set about designing and making the apparatus described below. Its design is based on a point of technique that does not seem to be much known, and to which, therefore, I should like to draw attention. If a glass tube be drawn out fine, sealed at one end, and evacuated, the sealed end may be broken under the surface of a liquid, which then flows in at any desired rate according to the diameter of the tube, and the tube may at any moment be fused off in the middle by a mouth blowpipe, without any inconvenience whatever. This process of filling with a liquid will I think be found advantageous in many cases. The only trouble about it is to get the capillary of the right bore; since the rate of flow depends on the fourth power of the radius it is easy to make the tube too wide or too narrow. Of course I made a good many failures at first, but after some practice could rely on getting the required condition. I used tubing of about 1 millim. internal diameter, and 4 millim. external, and drew it out till the internal diameter was about one sixth of a millimetre; a few centimetres of such a bore gives a convenient rate of flow for liquids of the viscosity of water.

The apparatus for vapour-pressure measurements is shown in fig. 1. It consists of a U-tube, A, to serve as a gauge, carrying a branch, B, below, drawn out for filling as mentioned above. The top of the gauge-tube is bent round each side to the bulbs C, C′, which are also provided with filling-tubes D, D′. The whole is shown flat in the diagram; but as a matter of fact the side tubes C D and C′ D′ were bent round till the bulbs nearly touched, to ensure their being of the same temperature. The apparatus was cleaned out with chromic acid, washed, and dried ; the capillaries were then drawn out and two of them sealed up, the third being left with the bit of wider tubing beyond the capillary untouched. By means of this it was attached to a mercury-pump, exhausted, and the capillary fused. The point B was then opened under mercury and fused off when the gauge contained sufficient : in the same way one of the bulbs was half filled with the mixture through D, and then the other with water (which must, of course, be freed from air) through D′. The apparatus, all of glass and hermetically sealed, is then ready for use : a glass millimetre scale is fastened with rubber bands to the gauge-tube, and the whole immersed in a large glass jar of

Fig. 1.



water. The scale was usually read by the telescope of a cathetometer, and sometimes the screw micrometer of the telescope was used to subdivide the graduation. The differential method avoids the necessity for any very great care in maintaining or measuring the temperature of the apparatus. It was found quite sufficient to heat the water-bath by leading a current of steam into it, and when the required temperature was reached, stop the steam for a moment and read the difference of level. When the highest temperature (90°) was reached, some of the water was siphoned off, replaced by cold, the whole mass well stirred, and a reading taken. There was no noticeable lag in the indications of the gauge, the readings at the same temperature, rising and falling, being in good agreement.

The fourth apparatus used was the Beckmann boiling-point apparatus, in its usual (second) form: with that observations at 100° were obtained of a kind to confirm the measurements made at somewhat lower temperatures with the vapour-pressure apparatus.

Observations of Vapour-pressure.

The following observations were obtained with the differential pressure-gauge: t is the temperature Centigrade, p the vapour-pressure of the mixture, π that of water; $\pi-p$ is therefore the difference observed with the gauge, and $(\pi-p)/\pi$ represents the relative lowering of the vapour-pressure of water by the addition of the quantity of phenol mentioned.

Phenol-water Mixtures.

67·36 per cent. of phenol.

t	50°	65°	75°	85°	90°
$\pi-p$	0·5	0·4	2·2	5·6	8·2
$(\pi-p)/\pi$	0·005	0·002	0·008	0·013	0·015

77·82 per cent. of phenol.

t	70°	75°	80°	85°	90°
$\pi-p$	2·6	5·0	8·2	12·5	17·1
$(\pi-p)/\pi$	0·011	0·017	0·023	0·029	0·032

82·70 per cent. of phenol.

t	40°	50°	60°	65°	70°	75°	80°	85°	90°
$\pi - p$	1·4	5·6	11·1	14·8	19·2	25·2	32·2	42·3	53·9
$(\pi - p)/\pi$	0·025	0·061	0·075	0·079	0·082	0·087	0·091	0·098	0·103

90·46 per cent. of phenol.

t	25°	40°	50°	60°	65°	70°	75°
$\pi - p$	1·9	9·1	17·5	31·7	43·2	53·5	68·6
$(\pi - p)/\pi$	0·081	0·165	0·190	0·213	0·231	0·230	0·237

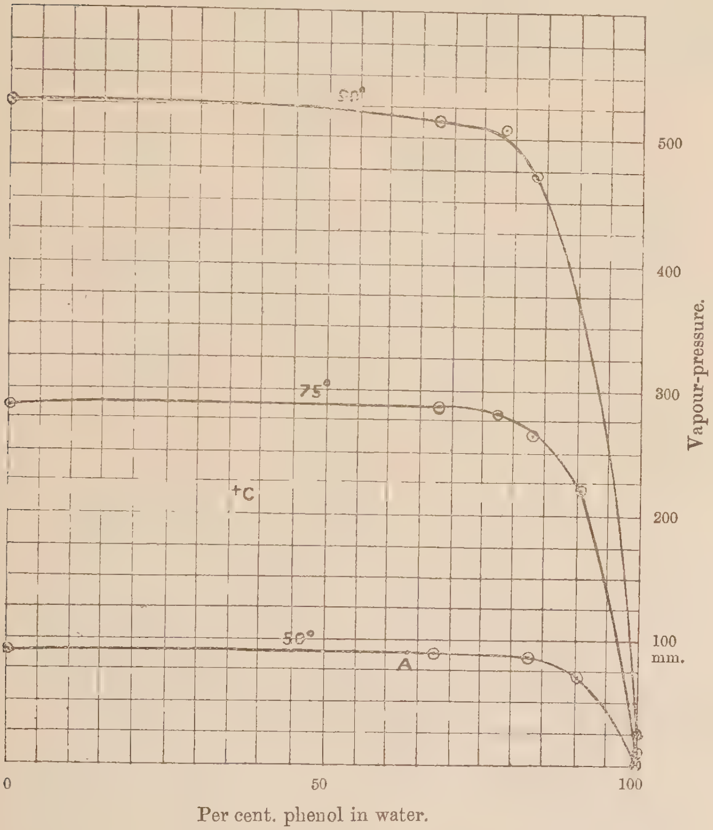
A mixture containing 7·74 per cent. of phenol gave no certain indication of a difference of pressure between the mixture and pure water. On this point, however, more reliable information is to be obtained with the Beckmann apparatus. It will be noticed from the preceding figures that the influence of the dissolved phenol becomes steadily greater as the temperature rises, *e.g.* 82 per cent. of phenol produces nearly twice as great a change of vapour-pressure proportionally at 90° as it does at 50°. In agreement with this the rise of vapour-pressures in dilute solutions of phenol is more marked at 100° than at the lower temperatures at which the vapour-pressure apparatus is available. The result of an experiment on the boiling-point is as follows:—

Per cent. phenol.	Fall of boiling-point.	Corresponding rise of vapour-pressure, $p - \pi$.
4·8	0·154	4·1
9·0	0·169	4·5
13·0	0·161	4·3
16·4	0·154	4·1

The general character of the results is sufficiently shown by fig. 2, in which the isothermals of 90° and 75° are sufficiently represented. That of 90° is comparable with the curve for alcohol-toluene mixtures (see fig. 2 in the preceding memoir), only that the flatness extending over a great part of the range of concentrations is exaggerated in the phenol-water mixtures. The curve for 75°—still above the critical point—

is still flatter; indeed it is imposible to say whether it rises or falls. Probably, therefore, below the critical point (where the vapour-pressure of phenol is inconveniently small for measurement) the isothermal, instead of consisting of a horizontal line bounded by two curves, would consist of a horizontal passing through the point representing pure water, bounded at the other end only by a descending curve. Such an isothermal—that of 50°—is shown in fig. 2. The horizontal part ends at the point A (63 per cent.), beyond which the mixtures are homogeneous : the curve beyond A may theoretically meet the horizontal line at a finite angle, but

Fig. 2.—Isothermals of Phenol-Water Mixtures.



that is certainly not distinguishable on the diagram. The curve is in fact exactly similar, so far as the experiments show, to that for 75°, and the pressure of the critical point, C on the diagram, which lies between them (at 68°·4) appears to make no difference whatever in this case—a case of great disparity in the vapour-pressures of the two components.

For comparison, a few experiments were made with aniline (not specially purified) and water. A mixture which consisted of two layers, even at the highest temperature used in the experiment, gave in the differential apparatus the following results :—

t	70°	80°	85°
$\pi - p$	$-6·8$	$-11·1$	$-13·3$
$(\pi - p)/\pi$ ...	$-0·0290$	$-0·0315$	$-0·0307$

Whilst the Beckmann apparatus gave at 100° :—

Per cent. aniline.	Lowering of boiling-point.	$\pi - p$.	$\frac{\pi - p}{\pi}$.
3·99	0·636	$-17·1$	0·0225
7·68	0 921	$-24·6$	0·0324
11·10	0·921	$-24·6$	0·0324

The second column gives the observed fall in temperature on adding aniline to the water; the third column the rise of pressure corresponding, at the rate of 26·8 millim. per degree. Water at 100° is saturated by the addition of 6·5 per cent. of aniline, and it will be seen that the vapour-pressure rises no further after that. The relative rise of vapour-pressure on saturation is 0·0324 at 100°, in satisfactory agreement with the numbers obtained by the differential gauge (0·0290, 0·0315, 0·0307), a tendency to increase with temperature being distinguishable here, as with phenol. Now suppose the vapour-pressure of a saturated mixture to be obtained in this way : let the partial pressure of the water-vapour be that of pure water reduced by the normal amount (Raoult's law) due to the solution in it of the maximum quantity of aniline : and let the partial pressure of aniline-vapour be that of pure aniline reduced by the normal amount due to the solution in it of the maximum quantity of water. We get the following results at 100° :—

Vapour-pressure of water = 760 millim.
Solubility of aniline = 6·5 per cent. = 1·32 molecular per cent.
Partial pressure of water = 98·68 per cent. of 760 = 749·9 millim.
Vapour-pressure of aniline = 46 millim.*
Solubility of water in aniline = 8·7 per cent. = 33 molecular per cent. (Alexejew).
Partial pressure of aniline = 30·8.
Total pressure = 749·9 + 30·8 = 780·7.
Observed pressure = 784·6 millim.

The vapour-pressure of the saturated mixture is therefore given fairly well by the above rule. The rule cannot be applied to phenol mixtures, as below the critical point the vapour-pressure of phenol is too low to determine with accuracy. Konowalow's measurements of the vapour-pressure of isobutyl alcohol-water mixtures, combined with Alexejew's measurements of solubility, give the following results. At 90° :—

Vapour-pressure of water = 525 millim.
Solubility of isobutyl alcohol = 7 per cent. = 1·8 molecular per cent.
Partial pressure of water-vapour = 98·2 per cent. of 525 = 515·5.
Vapour-pressure of isobutyl alcohol = 378 millim.
Solubility of water = 25 per cent. = 57·8 molecular per cent.
Partial pressure of isobutyl alcohol = 159·5.
Sum = 675·1.
Observed pressure = 767.

In this case the alcohol saturated with water contains more molecules of water than of alcohol, and it is not to be expected that the normal depression of the vapour-pressure should hold over so wide a range as 57·8 per cent. The numbers in fact show that the partial pressure of isobutyl alcohol must be very much greater—about 250 millim. The curve of partial pressures is therefore comparable with that for ethyl alcohol in benzene and toluene (see Part II. tables pp. 95–96).

---

* Kahlbaum, *Zeitsch. f. phys. Chem.* xxvi. p. 604.

Characteristic Surface for Phenol-Water Mixtures.

To complete an account of the behaviour of phenol-water mixtures, it is necessary to draw a diagram of the relations between temperature and concentration; this is given in

Fig. 3.

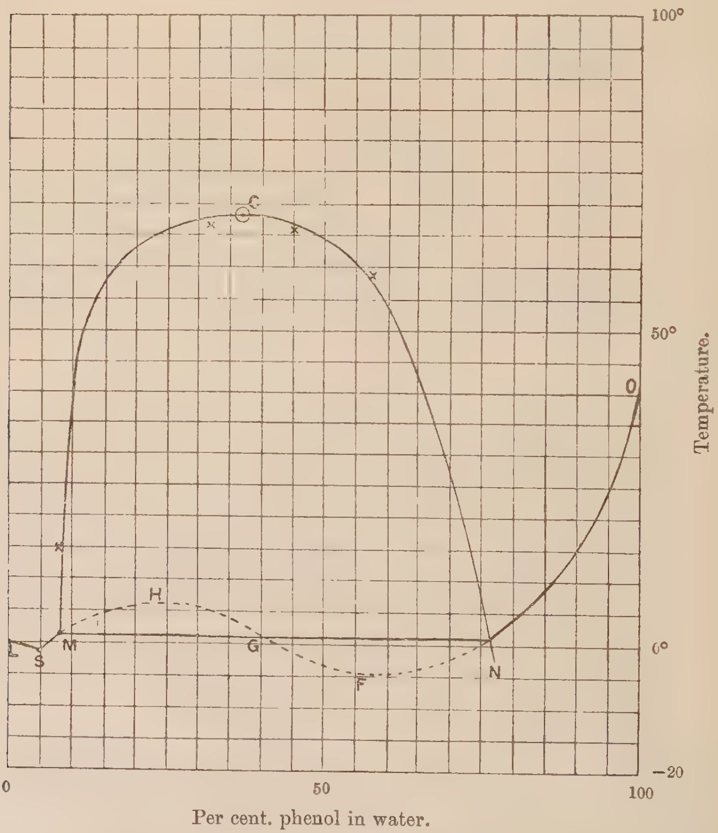


fig. 3. Figs. 2 and 3 together, therefore, give a notion of the shape of the "characteristic surface," *i. e.* the surface showing

the relations between concentration, temperature, and pressure. Fig. 2 contains three sections at right angles to the axis of temperature (for T=90°, T=75°, T=50° respectively), while fig. 3 gives one section at right angles to the axis of pressure ($p=1$ atmo).

The behaviour of phenol-water mixtures is formally identical with that of benzoic acid and water *, but the curve branches of the diagram are of very different relative sizes to those of the last-named mixtures. The features of the diagram are as follows :—

L. Freezing-point of water.
O. Freezing-point of phenol.
LS. Freezing-point of aqueous solutions of phenol.
ONFGHMS. Freezing-point of solutions of water in phenol.
S. Cryohydric point.
MC. Saturation of water with phenol.
NC. Saturation of (liquid) phenol with water.
C. Critical point of mixture.

The line LS is given by the thermodynamic equation

$$t=\frac{0{\cdot}02T^2}{L}$$

where T is the absolute temperature of fusion of ice, L the latent heat of fusion, and t the resulting molecular depression of the freezing-point ; it accordingly starts with a slope of 0°·2 for one per cent. of phenol. The initial slope of ON is given by a similar equation, and is 4°·15 for one per cent. of water ; a direct observation gave as a point of the curve

80·5 per cent. phenol,
melting-point + 5·0.

This is marked with a dot in the figure, and lies to the right of CN ; by continuing the curve through the point so found until CN is met, we reach the point N where the phenol is saturated with water ; on increasing the concentration a second liquid layer appears, consisting of water saturated with phenol. NFGHM is purely hypothetical, referring to unstable mixtures ; actually any mixture of concentration

---

* See van't Hoff, *Vorlesungen über theoretische und physikalische Chemie*, Heft i. p. 48. (Braunschweig, 1898.)

between 8 per cent. and 77 per cent. of phenol will separate into two layers on cooling, and on further reduction of temperature freeze at the constant temperature (about $+1^\circ{\cdot}5$) represented by the horizontal straight line MN. The cryohydric point lies to the left of the saturation curve CM, so that it is actually attainable: its existence was shown by making a solution containing 5·25 per cent. of phenol, and cooling it in a bath of ice and salt: it began to freeze without previous separation into two layers, and the temperature remained constant at $-0^\circ{\cdot}9$. About half of it was frozen, the beaker removed from the freezing-mixture, and some of the liquid remaining poured off for analysis; it was found to contain 4·83 per cent. phenol: this concentration is therefore in equilibrium with both ice and solid phenol which had been deposited on the sides of the beaker. The cryohydric mixture therefore contains so little phenol that it may be looked upon as a dilute solution of phenol in water, and its calculated freezing-point, according to van't Hoff's rule, would be $-1^\circ{\cdot}0$, in agreement with the observed value $-0^\circ{\cdot}9$. Consequently solutions of strength between M and S will deposit phenol on cooling, those between L and S (0 to 4·83 per cent.) ice.

The diagram is completed by the curve MCN which is drawn from Rothmund's observations*, which are indicated by dots; my own observations (shown by crosses) are in practical agreement with his and Alexejew's.

Finally, the curves divide the diagram into regions, with the following meanings:—

Below LS undercooled solutions of phenol, from which ice crystallizes out, with formation of the saturated solutions LS.

Below SMNO supersaturated solutions of phenol, from which phenol crystallizes out with formation of the saturated solutions of phenol in water (SM) and water in phenol (NO)

MCNGM, unstable mixtures which separate into the two saturated solutions CM and CN, forming two liquid layers.

Above LSMCNO homogeneous liquid mixtures.

The Davy-Faraday Research Laboratory, Royal Institution,
London, October, 1898.

---

[*] *L. c.* p. 452.

DISCUSSION.

Prof. S. YOUNG (communicated).—The fact pointed out by Mr. Lehfeldt that normal organic liquids always mix completely is a curious one. I should be inclined myself to qualify the statement by adding the words—"so far as our present knowlege goes."

At any rate there are certainly pairs of normal organic liquids which, though miscible in all proportions, approximate closely in their behaviour to partially miscible liquids.

Such a pair is benzene (B.P. 80°) and normal hexane (B.P. 69°).

When American petroleum is fractionally distilled it is found that the benzene, which is present in small quantity, does not come over at about 80° but mostly at about 65°, and the most probable explanation appeared to me to be that benzene and hexane behave, as regards distillation, like partially miscible liquids. This view has been fully confirmed by an investigation of the boiling-points and also the specific gravities of mixtures of the two hydrocarbons, an account of which has just been read before the Chemical Society by Dr. D. H. Jackson and myself.

The boiling-point curve is similar in general form to that of phenol and water, as shown by Mr. Lehfeldt, though the deviation from the ordinary form is not so marked.

10 % of benzene has practically no influence on the B.P. of normal hexane, but 10 % of hexane lowers the B.P. of benzene nearly 3°. Also there is always expansion on mixing benzene and hexane, the maximum reaching about 0·4 per cent.

Prof. S. P. THOMPSON asked whether any relation had been observed between the vapour-pressure and the surface-tension of the mixtures.

Dr. LEHFELDT, in reply, said he was not sure whether the surface-tensions of the components pass into one another at the critical point of mixture.

XXXII. *Longitudinal Vibrations in Solid and Hollow Cylinders.* *By* C. Chree, *Sc.D., LL.D., F.R.S.*[*]

Preliminary.

§ 1. The frequency $k/2\pi$ of longitudinal vibrations in the ideal isotropic bar of infinitely small cross section has long been known to be given by

$$k=p\sqrt{\mathrm{E}/\rho}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ρ is the density, E Young's modulus ; p is given by

$p=i\pi/l$ when the ends are both free or both fixed,

$p=(2i+1)\pi/(2l)$ when one end is free, the other fixed,

l being the length of the rod and i a positive integer.

For the fundamental or lowest note $i=1$.

For a circular bar whose radius a, though small compared to l, is not wholly negligible, the closer approximation

$$k=p(\mathrm{E}/\rho)^{\frac{1}{2}}\{1-\tfrac{1}{4}p^2\eta^2a^2\}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where η is Poisson's ratio, was obtained independently by Prof. Pochhammer [†] and Lord Rayleigh[‡] fully 20 years ago.

§ 2. The subject has been treated by myself in three papers in the 'Quarterly Journal of . . . Mathematics' (A) (p. 287, 1886), (B) (p. 317, 1889), (C) (p. 340, 1890).

In (A) I arrived at (2) describing it (*l. c.* p. 296) as "obtained as a second approximation by Lord Rayleigh." I further said, "We do not think, however, that his proof affords any means of judging of the degree of accuracy of the result, as it is founded on a more or less probable hypothesis and does not profess to be rigid." I subsequently learned that Lord Rayleigh did not admit any want of rigidity in his proof, and it appears without modification in the second edition of his Treatise on 'Sound.' I much regret having to differ from so eminent an authority, but I have not altered my original opinion.

---

[*] Read December 9, 1898.

[†] *Crelle*, vol. lxxxi. (1876).

[‡] 'Theory of Sound,' vol. i. art. 157.

In (B) I reached the more general result

$$k=p(\mathrm{E}/\rho)^{\frac{1}{2}}(1-\tfrac{1}{2}p^2\eta^2\kappa^2), \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where κ is the radius of gyration of the cross section of the rod about its axis. This was established by a strict elastic solid method for an elliptic section, and in a somewhat less rigid way for a rectangular section. (A) and (B) were confined, like the investigations of Lord Rayleigh and Professor Pochhammer, to isotropic materials.

In (C) I considered the more general case of an æolotropic bar whose long axis was an axis of material symmetry, and found by strict elastic solid methods that (2) still held for a circular section, if E denoted Young's modulus for stress along the length of the bar, and η Poisson's ratio for the consequent perpendicular contractions. Further, applying Lord Rayleigh's method, modified in a way I deem necessary, I obtained (3) for any form of cross section.

§ 3. Since the publication of (C) Mr. Love has discussed the subject in vol. ii. of his 'Treatise on Elasticity.' On his p. 119* he refers to (2) as "first given by Prof. Pochhammer... and afterwards apparently independently by Mr. Chree." Again, in the new edition of his 'Sound' Lord Rayleigh, after deducing (2), says "A more complete solution... has been given by Pochhammer... A similar investigation has also been published by Chree."

In view of these remarks, I take this opportunity of stating explicitly :—

1. That Pochhammer's work was wholly unknown to me until the appearance of Love's 'Elasticity.'

2. That my method of solution in (A) is essentially different from Pochhammer's, while the methods in (B) and (C) are absolutely different from his. The method of (A) agrees with Pochhammer's in employing the equations of elasticity in cylindrical coordinates. After obtaining, however,—as is customary in most elastic problems—the differential equation for the dilatation, Pochhammer obtains a differential equation for the quantity

$$\frac{1}{2}\left(\frac{du}{dz}-\frac{dw}{dr}\right),$$

---

* The preface, p. 13, describes the result as "obtained independently' by me.

u and w being the displacements parallel to the radius r and the axis z, and uses this quantity as a stepping-stone to the values of u and w. On the other hand, I succeeded in separating u and w so as to obtain at once two differential equations, in one of which u appeared alone with the dilatation, while the other contained only w and the dilatation (see (28) and (29) later).

§ 4. There are two other points in Mr. Love's Treatise to which I should like to refer. In his art. 263 he substitutes the term *extensional* for *longitudinal*, adding in explanation, "The vibrations here considered are the 'longitudinal' vibrations of Lord Rayleigh's *Theory of Sound*. We have described them as 'extensional,' to avoid the suggestion that there is no lateral motion of the parts of the rod."

I am altogether in sympathy with the object which Mr. Love has in view (I expressed myself somewhat strongly on the point in (A) p. 296, and (C) pp. 351–2), but I doubt the wisdom of attempting to displace a term so generally adopted as *longitudinal*.

In the second matter I regret to find myself at variance with Mr. Love. Referring to transverse vibrations in a rod, he says on p. 124 of his vol. ii., "the boundary conditions at free ends cannot be satisfied exactly . . . as they can in the . . . extensional (longitudinal) modes." In reality, however, the boundary equations at a free end are not exactly satisfied in the case of longitudinal vibrations either by Pochhammer's solution or my own. The slip may be a purely verbal one on Mr. Love's part, but his readers might be led to accept the statement as accurate, owing to a slight error in the expression for the shearing stress $\widehat{zr}$ near the top of Mr. Love's p. 120. We find there

$$\widehat{zr} = 2\mu\{\gamma \mathrm{A} \frac{d}{dr} \mathrm{J}_0(\kappa' r) + \ldots\} e^{\iota(\gamma z + pt)},$$

where $\qquad \iota \equiv \sqrt{-1}.$

The correct expression (compare Mr. Love's second boundary equation on p. 118) is

$$\widehat{zr} = \iota\mu\{2\gamma \mathrm{A} \frac{d}{dr} \mathrm{J}_0(\kappa' r) + \ldots\} e^{\iota(\gamma z + pt)}.$$

Owing to the omission of ι in the expression on p. 120 it looks as if $\widehat{zr}$ vanished for the same values of z as the normal stress $\widehat{zz}$. In reality, as I showed in (A) p. 295, $\widehat{zr}$ does not vanish over a terminal free section of radius a, but is of the order $r(r^2-a^2)/l^3$, where r is the perpendicular on the axis. We are quite justified in neglecting $\widehat{zr}$ when terms of order $(a/l)^3$ are negligible, but strictly speaking the solution is so far only an approximate one when the ends are free.

A New Method.

§ 5. In the Camb. Phil. Soc. Trans. vol. xv. pp. 313–337 I showed how the mean values of the strains and stresses might be obtained in any elastic solid problem independently of a complete solution. For isotropic materials I obtained (*l. c.* p. 318) three formulæ of the type

$$\mathrm{E}\iiint \frac{d\gamma}{dz}\,dx\,dy\,dz = \iiint \{\mathrm{Z}z-\eta(\mathrm{X}x+\mathrm{Y}y)\}\,dx\,dy\,dz$$

$$+\iint \{\mathrm{H}z-\eta(\mathrm{F}x+\mathrm{G}y)\}\,d\mathrm{S}, \quad . \quad (4)$$

where α, β, γ are components of displacement, X, Y, Z of bodily forces, and F, G, H of surface forces. The volume integrals extend throughout the entire volume, and the surface integrals over the entire surface of the solid. As was explicitly stated in proving the results (*l. c.* p. 315), X, Y, Z may include 'reversed effective forces'

$$-\rho\frac{d^2\alpha}{dt^2}, \quad -\rho\frac{d^2\beta}{dt^2}, \quad -\rho\frac{d^2\gamma}{dt^2},$$

where ρ is the density.

In the present application there are no real bodily forces; we may also leave surface forces out of account, if we suppose that when one end of a rod is held, that end lies in the plane $z=0$.

Supposing the rod to vibrate with frequency $k/2\pi$, we have

$$\mathrm{X}=-\rho\frac{d^2\alpha}{dt^2}=k^2\rho\alpha, \text{ \&c.},$$

so that we replace (4) by

$$E\iiint \frac{d\gamma}{dz}\,dx\,dy\,dz = k^2\rho \iiint \{\gamma z - \eta(\alpha x + \beta y)\}\,dx\,dy\,dz, \quad . \quad (5)$$

and similarly with the two other equations of the same type.

The only other result required is one established in my paper (B): viz., that the general solution of the elastic solid equations of motion in which the terms contain $\cos pz$ or $\sin pz$ consists of two independent parts. In the first, which alone applies to longitudinal vibrations, α and β are odd and γ an even function of x and y.

We may thus assume

$$\left.\begin{aligned} \alpha &= \cos kt \cos(pz-\epsilon)\{A_1x + A_1'y + A_3x^3 + A_3'x^2y \\ &\qquad + A_3''xy^2 + A_3'''y^3 + \ldots\}, \\ \beta &= \cos kt \cos(pz-\epsilon)\{B_1x + B_1'y + B_3x^3 + \ldots\}, \\ \gamma &= \cos kt \sin(pz-\epsilon)\{C_0 + C_2x^2 + C_2'xy + C_2''y^2 + \ldots\}, \end{aligned}\right\} \quad . \quad (6)$$

where ϵ is a constant depending on the position of the origin of coordinates and the terminal conditions. It is obvious from various considerations that the same ϵ occurs in the values of α, β, γ. Certain relations must subsist between the constants A, B, C in the above expressions, in virtue of the body-stress equations, but we do not require to take any heed of these for our present purpose.

§ 6. As the validity of solutions in series has been a subject of contention in other elastic solid problems, some doubt may be entertained as to the results (6). I would be the last to deny the reasonableness of this, because I do not myself regard (6) as universally applicable.

According to my investigations, quantities such as (A_3x^3/A_1x) are of the order (greatest diameter/nodal length)^2, and the series become less rapidly convergent as (greatest diameter/nodal length) increases. In other words, increase either in (greatest diameter/rod length) or in the order of the "harmonic" of the fundamental note reduces the rapidity of convergence. The proper interpretation, however, to put on this is not that (6) is a wrong formula for *longitudinal* vibrations, but simply that under the conditions specified the vibrations tend to depart too widely from the longitudinal type. If we apply this solution the results deduced from it themselves tend to show the degree of rapidity of the convergence, and what we have to do is to keep our eye on the results and accept them only so long as they are consistent with rapid convergency.

Perhaps the following *résumé* of my views on this point may be useful :—

1°. In obtaining (6) originally I employed the *complete* elastic solid equations for isotropic materials. In other cases where difficulties have arisen over expansion in series, they seem mainly due to the fact that the elastic solid equations have been whittled down in the first instance for purposes of simplicity. When one omits terms in a differential equation for diplomatic reasons, the results may be perfectly satisfactory under certain limitations. Owing, however, to the mutilation of the differential equations, the resulting solutions are unlikely to contain within themselves any satisfactory indication of the limits to their usefulness. It is very much a case of running a steam-engine without a safety-valve.

2°. When the bar is of circular section and isotropic, the series occurring in (6) are Bessel's functions of a well-known type, whose rapidity of convergence appears well ascertained under the normal conditions of the problem. When the section is circular, and the material not isotropic but symmetrical round the axis, the series, whose mathematical law of development I have obtained, converge to all appearance quite as rapidly as in the case of isotropy. The other cases of isotropic material—sections elliptical or rectangular—which I have considered present similar features ; the only difference being that the rate of convergence diminishes with increase in any one dimension of the cross section.

3°. If we suppose $k=0$, or the vibrations to be of infinite period, the solution must reduce to that for the equilibrium of a rod under uniform longitudinal traction. Now, in the case of equilibrium γ/z reduces to a constant, while α and β are linear in x and y for *all forms of cross section*. The commencing terms in series (6) are thus of the proper form under all conditions, and the form of the differential equations shows that if α, for instance, contains a term in x it must contain terms in x^3, xy^2, and other *integral* powers of x and y.

4°. The general type of the differential equations is the same for all kinds of elastic material, isotropic or æolotropic, and the surface conditions are identical in all cases; thus the type of solution must always be the same. The results may become enormously lengthy for complicated kinds of æolotropy, but by putting a variety of the elastic constants equal to one another we must reduce the most complicated of these expressions to coincidence with the corresponding results for isotropy. Of course it does not follow that the convergence will be equally rapid for all materials. A large value of a Poisson's ratio in conjunction with an elongated dimension of the cross section may reduce the convergency so much as to throw the higher "harmonics" outside the pale of longitudinal vibrations.

5°. The more the section departs from the circular form the less rapid in general is the convergence, and the larger the correction supplied by the second approximation. In fact the size of the correction is probably the best criterion by which to judge of the limitations of our results. If the correction is large even for the fundamental note, it is pretty safe to conclude that the section is not one adapted for the ordinary type of longitudinal vibrations. If a section, for instance, were of an acutely stellate character, with a lot of rays absent and the centroid external to the material, I for one should be extremely chary of applying to it the ordinary formula.

§ 7. For definiteness let us consider the fixed-free vibrations, taking the origin of coordinates at the centroid of the fixed end. Our terminal conditions are

$$\gamma=0 \text{ when } z=0,$$

$$\widehat{zz}=0 \quad ,, \quad z=l;$$

the latter condition being the same thing as

$$\frac{d\gamma}{dz}=0 \text{ when } z=l.$$

These conditions give at once

$$\epsilon=0, \quad p=(2i+1)\pi/2l,$$

and hence

$$\int_0^l pz\sin(pz-\epsilon)dz=\int_0^l \cos(pz-\epsilon)dz.$$

Take the axes of x and y along the principal axes of the cross section σ, so that

$$\iint xy\,dx\,dy=0,$$

$$\iint x^2dx\,dy=\kappa_2{}^2\sigma,\quad \iint y^2dx\,dy=\kappa_1{}^2\sigma.$$

Then, substituting from (6) in (5), we obtain at once

$$(\mathrm{E}p-k^2\rho/p)(\mathrm{C}_0+\mathrm{C}_2\kappa_2{}^2+\mathrm{C}_2{}''\kappa_1{}^2+\ldots)$$
$$=-k^2\rho\eta(\mathrm{A}_1\kappa_2{}^2+\mathrm{B}_1{}'\kappa_1{}^2+\ldots)\quad .\quad .\quad (7)$$

The section is supposed small, *i. e.* terms in $\kappa_1{}^2$, $\kappa_2{}^2$ are small compared to C_0, though large compared to the terms of orders $\kappa_1{}^4$, &c., which are omitted in the above equation. Thus as a first approximation the coefficient of C_0 must vanish, or

$$k=p\sqrt{\mathrm{E}/\rho},\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad (1)$$

which is simply the ordinary frequency equation.

Treating the other two equations of the type (5) similarly, we obtain the two results

$$\mathrm{E}(\mathrm{A}_1+3\mathrm{A}_3\kappa_2{}^2+\mathrm{A}_3{}''\kappa_1{}^2+\ldots)$$
$$=-k^2\rho\left\{\frac{\eta}{p}(\mathrm{C}_0+\mathrm{C}_2\kappa_2{}^2+\mathrm{C}_2{}''\kappa_1{}^2+\ldots)+\eta\mathrm{B}_1{}'\kappa_1{}^2-\mathrm{A}_1\kappa_2{}^2+\ldots\right\},\ (8)$$

$$\mathrm{E}(\mathrm{B}_1{}'+\mathrm{B}_3{}'\kappa_2{}^2+3\mathrm{B}_3{}'''\kappa_1{}^2+\ldots)$$
$$=-k^2\rho\left\{\frac{\eta}{p}(\mathrm{C}_0+\mathrm{C}_2\kappa_2{}^2+\mathrm{C}_2{}''\kappa_1{}^2+\ldots)+\eta\mathrm{A}_1\kappa_2{}^2-\mathrm{B}_1{}'\kappa_1{}^2+\ldots\right\}.\ (9)$$

The terms not shown are of the order $\kappa_1{}^4$, $\kappa_2{}^4$, or higher powers of κ_1 and κ_2. Combining (8) and (9) we get

$$\mathrm{E}(\mathrm{A}_1-\mathrm{B}_1{}')=k^2\rho(1+\eta)(\mathrm{A}_1\kappa_2{}^2-\mathrm{B}_1{}'\kappa_1{}^2)+\ldots,\quad .\quad .\quad (10)$$

$$\mathrm{E}(\mathrm{A}_1+\mathrm{B}_1{}')=-2k^2\rho(\eta/p)(\mathrm{C}_0+\mathrm{C}_2\kappa_2{}^2+\mathrm{C}_2{}''\kappa_1{}^2+\ldots)$$
$$+(1-\eta)k^2\rho(\mathrm{A}_1\kappa_2{}^2+\mathrm{B}_1{}'\kappa_1{}^2)+\ldots\quad .\quad (11)$$

To see the significance of (10) replace $k^2\rho$ by its approximate value $p^2\mathrm{E}$, when we have

$$\mathrm{A}_1-\mathrm{B}_1{}'=(1+\eta)\{\mathrm{A}_1(p\kappa_2)^2-\mathrm{B}_1{}'(p\kappa_1)^2\}+\ldots\quad .\quad (12)$$

As we have seen, $p=(i+\frac{1}{2})\pi/l$; and thus, so long as i is not too large, $(p\kappa_2)^2$ and $(p\kappa_1)^2$ are in a thin rod small quantities of the orders $(\kappa_2/l)^2$ and $(\kappa_1/l)^2$. Hence we deduce from (12) as a first approximation

$$B_1'=A_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

This is all we require for our present purpose; but, in passing, it may be noted that as a second approximation we have

$$B_1'=A_1\{1+(1+\eta)p^2(\kappa_1^2-\kappa_2^2)\}.$$

The more the section departs from circularity—*i.e.* the more elongated it is in one direction—the greater is the difference between B_1' and A_1. This and the fact that $i\kappa_1/l$ and $i\kappa_2/l$ must both remain small are useful indications of the limitations implied in the method of solution.

Employing (13) in (7) and (11) we have, neglecting smaller terms,

$$(Ep-k^2\rho/p)(C_0+C_2\kappa_2^2+C_2''\kappa_1^2)=-k^2\rho\eta A_1(\kappa_2^2+\kappa_1^2),$$
$$2k^2\rho(\eta/p)(C_0+C_2\kappa_2^2+C_2''\kappa_1^2)=-2EA_1.$$

Whence we deduce at once, without knowing anything of the constants C_2, A_3, &c.,

$$(Ep-k^2\rho/p)\div(2k^2\rho\eta/p)=k^2\rho\eta(\kappa_2^2+\kappa_1^2)/(2E).$$

Using in the small term (that containing k^4) the first approximation (1), we have

$$k^2\rho=E\,p^2\{1-\eta^2p^2(\kappa_1^2+\kappa_2^2)\}; \quad . \quad . \quad . \quad (14)$$

and this, as

$$\kappa_1^2+\kappa_2^2=\kappa^2,$$

simply reduces to (3).

That the above proof is as satisfactory in every way as one based on ordinary elastic solid methods I should hesitate to maintain. Unless one knew beforehand a good deal about the problem there would, I fear, be considerable risk of misadventure.

§ 8. In illustrating the method in detail I have selected the case of isotropic material simply because I did not wish to frighten my readers. The assumption of isotropy almost invariably shortens the mathematical expressions, and generally also simplifies the character of the mathematical operations; and isotropic solids thus flourish in the text-books to a much greater degree than they do in nature. When, however, the mathematical difficulties are trifling, as in the present case, it seems worth while considering some less specialized material. I shall thus briefly indicate the application of the method to the case of material symmetrical with respect to the three rectangular planes of x, y, z, taken as in the previous example. In this case the stress-strain relations involve, on the usual hypothesis, nine elastic constants. Such quantities as Young's modulus or Poisson's ratio must be defined by reference to directions. Thus let E_1, E_2, E_3 denote the three principal Young's moduli, the directions 1, 2, 3 being taken along the axes of x, y, z respectively. There are six corresponding Poisson's ratios, each being defined by two suffixes, the first indicating the direction of the longitudinal pull, the second that of the contraction. For instance, η_{12} applies in the case of the contraction parallel to the y-axis due to pull parallel to the x-axis. The order of the suffixes is not immaterial, but there exist the following relations :—

$$\eta_{12}/E_1=\eta_{21}/E_2\ ; \quad \eta_{23}/E_2=\eta_{32}/E_3\ ; \quad \eta_{31}/E_3=\eta_{13}/E_1. \quad (15)$$

The three equations answering to (4) are

$$E_3\iiint\frac{d\gamma}{dz}\,dz\,dy\,dz=k^2\rho\iiint\{\gamma z-\eta_{31}\alpha x-\eta_{32}\beta y\}\,dx\,dy\,dz, \quad (16)$$

$$E_1\iiint\frac{d\alpha}{dx}\,dx\,dy\,dz=k^2\rho\iiint\{ax-\eta_{12}\beta y-\eta_{13}\gamma z\}\,dx\,dy\,dz, \quad (17)$$

$$E_2\iiint\frac{d\beta}{dy}\,dx\,dy\,dz=k^2\rho\iiint\{\beta y-\eta_{23}\gamma z-\eta_{21}\alpha x\}\,dx\,dy\,dz. \quad (18)$$

From the nature of the elastic solid equations the expressions for the displacements must be of the same general form as for isotropy, so that we may still apply the formulæ (6) for α, β, γ. Doing so, and following exactly the same procedure as in the case of isotropy, we obtain from (16), for any shape of section,

$$(E_3p-k^2\rho/p)(C_0+\ldots)=-k^2\rho(\eta_{31}A_1\kappa_2^2+\eta_{32}B_1'\kappa_1^2)+\ldots, \quad (19)$$

and from (17) and (18) as first approximations

$$A_1/(\eta_{13}E_3/E_1)=B_1'/(\eta_{23}E_3/E_2)=-p(C_0+\ldots). \quad . \quad (20)$$

Thence we obtain at once

$$k^2\rho = p^2 \mathrm{E}_3 \left\{ 1 - p^2 \mathrm{E}_3 \left(\frac{\eta_{31}\eta_{13}}{\mathrm{E}_1} \kappa_2{}^2 + \frac{\eta_{32}\eta_{23}}{\mathrm{E}_2} \kappa_1{}^2 \right) \right\}. \qquad (21)$$

Employing (15) we give this the more elegant form

$$k^2\rho = p^2 \mathrm{E}_3 \{ 1 - p^2 (\eta_{31}{}^2 \kappa_2{}^2 + \eta_{32}{}^2 \kappa_1{}^2) \},$$

whence

$$k = p(\mathrm{E}_3/\rho)^{\frac{1}{2}} \{ 1 - \tfrac{1}{2} p^2 (\eta_{31}{}^2 \kappa_2{}^2 + \eta_{32}{}^2 \kappa_1{}^2) \}. \quad . \quad (22)$$

For a circular section of radius a

$$k = p(\mathrm{E}_3/\rho)^{\frac{1}{2}} \{ 1 - \tfrac{1}{8} p^2 a^2 (\eta_{31}{}^2 + \eta_{32}{}^2) \}. \quad . \quad . \quad (23)$$

For a rectangular section $2a \times 2b$, the side $2a$ being parallel to the x-axis,

$$k = p(\mathrm{E}_3/\rho)^{\frac{1}{2}} \{ 1 - \tfrac{1}{6} p^2 (a^2 \eta_{31}{}^2 + b^2 \eta_{32}{}^2) \}. \quad . \quad . \quad (24)$$

For a given size and shape of rectangle, the correction to the first approximation is largest when the longer side is that answering to the larger Poisson's ratio (for traction along the rod). Possibly experimental use might be made of this result in examining materials for æolotropy.

If the material, though not isotropic, be symmetrical in structure round lines parallel to the length of the rod,

$$\eta_{31} = \eta_{32} = \eta, \text{ say},$$

and writing E for E_3 in (22) we reproduce the result (60) of paper (C).

The results (22), (23), and (24), so far as my knowledge goes, are absolutely new.

Extension of Earlier Results.

§ 9. My paper (A), like the corresponding investigation of Pochhammer, dealt only with a solid circular cylinder; but the same method is applicable to a hollow circular cylinder. For greater continuity I shall employ in the remainder of this paper the notation of paper (A).

The displacements are u outwards along r, the perpendicular on the axis, and w parallel to the axis, taken as that of z. Thomson and Tait's notation m, n for the elastic constants is employed. The frequency is $k/2\pi$ and the density ρ, as in the earlier part of this paper, and for brevity

$$k^2\rho/(m+n) = \alpha^2, \quad k^2\rho/n = \beta^2, \quad . \quad . \quad . \quad (25)$$

so that α and β have utterly different significations from their previous ones.

There being no displacement perpendicular to r, in a transverse section, the dilatation δ is given by

$$\delta = \frac{du}{dr} + \frac{u}{r} + \frac{dw}{dz}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

It was shown in paper (A) that the following equations held

$$\frac{d^2\delta}{dr^2} + \frac{1}{r}\frac{d\delta}{dr} + \frac{d^2\delta}{dz^2} + \alpha^2\delta = 0, \quad . \quad . \quad . \quad . \quad (27)$$

$$\frac{d^2u}{dr^2} + \frac{1}{r}\frac{du}{dr} - \frac{u}{r^2} + \frac{d^2u}{dz^2} + \beta^2 u = -\frac{m}{n}\frac{d\delta}{dr}, \quad (28)$$

$$\frac{d^2w}{dr^2} + \frac{1}{r}\frac{dw}{dr} + \frac{d^2w}{dz^2} + \beta^2 w = -\frac{m}{n}\frac{d\delta}{dz}. \quad . \quad (29)$$

Employing J and Y to represent the two solutions of Bessel's equation we find, as in paper (A), that the above equations are satisfied by

$$\delta = \cos kt \cos(pz-\epsilon)\left\{CJ_0(r(\alpha^2-p^2)^{\frac{1}{2}}) + C'Y_0(r(\alpha^2-p^2)^{\frac{1}{2}})\right\}, (30)$$

$$u = \cos kt \cos(pz-\epsilon)\Big[AJ_1(r(\beta^2-p^2)^{\frac{1}{2}}) + A'Y_1(r(\beta^2-p^2)^{\frac{1}{2}})$$
$$-\frac{m}{n}\frac{(\alpha^2-p^2)^{\frac{1}{2}}}{\alpha^2-\beta^2}\left\{CJ_1(r(\alpha^2-p^2)^{\frac{1}{2}}) + C'Y_1(r(\alpha^2-p^2)^{\frac{1}{2}})\right\}\Big], \quad . \quad (31)$$

$$w = -\cos kt \sin(pz-\epsilon)\Big[\left\{AJ_0(r(\beta^2-p^2)^{\frac{1}{2}}) + A'Y_0(r(\beta^2-p^2)^{\frac{1}{2}})\right\}$$
$$\times\frac{(\beta^2-p^2)^{\frac{1}{2}}}{p} + \frac{mp}{n(\alpha^2-\beta^2)}\left\{CJ_0(r(\alpha^2-p^2)^{\frac{1}{2}}) + C'Y_0(r(\alpha^2-p^2)^{\frac{1}{2}})\right\}\Big], (32)$$

where A, A′, C, C′ are arbitrary constants to be determined by the surface conditions.

In reality α^2-p^2 is negative; but the properties of the J and Y Bessel functions which at present concern us are not affected thereby. β^2-p^2, on the other hand, is positive.

§ 10. If a and b are the radii of the outer and inner cylindrical surfaces respectively, then from the conditions which hold over these surfaces we must have

$$\frac{du}{dz}+\frac{dw}{dr}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (33)$$

$$(m-n)\delta+2n\frac{du}{dr}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (34)$$

when $r=a$, and when $r=b$.

As regards the terminal conditions we should have, following the ordinary view of longitudinal vibrations,

$$w=0 \text{ over a fixed end}, \quad . \quad . \quad . \quad . \qquad (35)$$

$$\left.\begin{aligned}\widehat{zz}&\equiv(m-n)\delta+2n\frac{dw}{dz}=0,\\ \widehat{zr}&\equiv n\left(\frac{du}{dz}+\frac{dw}{dr}\right)=0\end{aligned}\right\}\text{over a free end.} \qquad (36)$$

We have no means of satisfying these terminal equations by means of the present solution save by selecting suitable values for p and ϵ. Clearly if both ends $z=0$ and $z=l$ be fixed we accomplish our object by putting

$$\epsilon=0, \quad p=i\pi/l.$$

If, however, $z=l$ be a free end, while $z=0$ is a fixed, we must have $\epsilon=0$ to satisfy the conditions of the fixed end; and this leaves us with

$$\widehat{zz}\propto\cos pl,$$

$$\widehat{zr}\propto\sin pl$$

over the free end. This is the difficulty we have already indicated in § 4; and it is in no respect peculiar to hollow cylinders, and need not further concern us at present.

§ 11. In dealing with the surface conditions, brevity is effected by the use of the notation

$$\lambda\equiv\sqrt{\alpha^2-p^2}, \qquad \mu\equiv\sqrt{\beta^2-p^2}, \quad . \quad . \qquad (37)$$

whence

$$\alpha^2-\beta^2=\lambda^2-\mu^2.$$

After simplifications, into which I need not enter, the elimination of A, A′, C, C′ from the four equations holding over the cylindrical surface supplies the determinantal equation

$$\begin{vmatrix} J_1(a\mu) & Y_1(a\mu) & -\frac{2p^2\lambda}{a^2(\mu^2-p^2)}J_1(a\lambda) & -\frac{2p^2\lambda}{a^2(\mu^2-p^2)}Y_1(a\lambda) \\ J_1(b\mu) & Y_1(b\mu) & -\frac{2p^2\lambda}{a^2(\mu^2-p^2)}J_1(b\lambda) & -\frac{2p^2\lambda}{a^2(\mu^2-p^2)}Y_1(b\lambda) \\ J_1'(a\mu) & Y_1'(a\mu) & \frac{m-n}{2n\mu}J_0(a\lambda)+\frac{\lambda^2}{a^2\mu}J_1'(a\lambda) & \frac{m-n}{2n\mu}Y_0(a\lambda)+\frac{\lambda^2}{a^2\mu}Y_1'(a\lambda) \\ J_1'(b\mu) & Y_1'(b\mu) & \frac{m-n}{2n\mu}J_0(b\lambda)+\frac{\lambda^2}{a^2\mu}J_1'(b\lambda) & \frac{m-n}{2n\mu}Y_0(b\lambda)+\frac{\lambda^2}{a^2\mu}Y_1'(b\lambda) \end{vmatrix} = 0. \quad (38)$$

This equation is true irrespective of the *relative* magnitudes of a and b. It constitutes a frequency equation supplying values of k which apply to the type of vibrations consistent with the surface conditions. If both ends of the rod be fixed there is no restriction to the absolute values of a/l and b/l; but if one or both ends are free, such a restriction is really involved in the fact that unless ia/l and ib/l be both small—i being the order of the harmonic of the fundamental note under consideration—the failure to satisfy exactly the terminal condition

$$zr=0$$

involves an inconsistency which cannot be allowed.

§ 12. The case of a thick rod fixed at both ends is of little physical interest, and the treatment of (38) in its utmost generality would involve grave mathematical difficulties. I thus limit my attention to the case when ia/l and ib/l are both small. This implies that $a\lambda$, $b\lambda$, $a\mu$, and $b\mu$ are all small. Thus in dealing with the various Bessel functions we may use the following approximations*, which hold so long as the variable x is small,

$$\left.\begin{aligned} J_0(x)&=1-x^2/4, \\ J_1(x)&=\tfrac{1}{2}x(1-x^2/8), \\ J_1'(x)&=\tfrac{1}{2}(1-\tfrac{3}{8}x^2), \\ Y_0(x)&=(1-x^2/4)\log x+x^2/4, \\ Y_1(x)&=\frac{x}{2}(1-x^2/8)\log x-x^{-1}-x/4, \\ Y_1'(x)&=\tfrac{1}{2}(1-\tfrac{3}{8}x^2)\log x+x^{-2}+\tfrac{1}{4}. \end{aligned}\right\} \quad . \quad . \quad (39)$$

Retaining only the principal terms in (38), we are of course led at once to the first approximation (1). Again, if (1) held exactly we should find

---

* *Cf.* Gray and Mathews' 'Treatise on Bessel Functions,' pp. 11, 22, &c.

$$\left.\begin{aligned}\alpha^2&=p^2n(3m-n)\div m(m+n),\\ \lambda^2&=-p^2(m-n)^2\div m(m+n),\\ \mu^2-p^2&=p^2(m-n)/m;\end{aligned}\right\}\quad . \quad . \quad (40)$$

and to a first approximation

$$-\frac{\mathrm{J}_1(a\lambda)}{\mathrm{J}_1(a\mu)}\,\frac{2p^2\lambda}{\alpha^2(\mu^2-p^2)}=-\frac{2p^2\lambda^2}{\alpha^2\mu(\mu^2-p^2)}=\frac{2}{\mu}\,\frac{m(m-n)}{n(3m-n)},$$

$$\frac{m-n}{2n\mu}\,\frac{\mathrm{J}_0(a\lambda)}{\mathrm{J}_1'(a\mu)}+\frac{\lambda^2}{\alpha^2\mu}\,\frac{\mathrm{J}_1'(a\lambda)}{\mathrm{J}_1'(a\mu)}=\frac{2(m-n)}{2n\mu}+\frac{\lambda^2}{\alpha^2\mu}=\frac{2m(m-n)}{\mu n(3m-n)},$$

and similarly if a be replaced by b.

We thus see that the third column in the determinant (38) is such that each principal term in it is obtained by multiplying the principal term in the same row in the first column by the same constant $2m(m-n)\div\{\mu n(3m-n)\}$. Now if one column of a determinant is obtainable by multiplying another column by a constant that determinant vanishes. It is thus at once clear that in proceeding even to a second approximation we need retain only the principal terms in the second and fourth columns of (38). This removes what seemed at first sight a formidable obstacle, viz. the occurrence of the logs in the expressions for Y_0, Y_1, and Y_1'.

§ 13. For further simplification of the determinant multiply each term by 2, and divide the first and second rows by $a\mu$ and $b\mu$ respectively. Then for the second row write the difference between the first and second rows, and for the fourth row the difference between the third and fourth rows, and multiply the resulting rows by $b^2/(a^2-b^2)$. Finally multiply the second column by $a^2\mu^2/2$, the third column by $\mu\alpha^2$, and the fourth column by $a^2\mu\alpha^2/2$. We thus reduce (38) to the easily manageable form

$$\begin{vmatrix} 1-\frac{1}{8}a^2\mu^2 & -1 & -\dfrac{2\lambda^2p^2}{\mu^2-p^2}\left(1-\frac{1}{8}a^2\lambda^2\right) & \dfrac{2p^2}{\mu^2-p^2}\\ \frac{1}{8}b^2\mu^2 & -1 & -\dfrac{\lambda^4p^2b^2}{4(\mu^2-p^2)} & \dfrac{2p^2}{\mu^2-p^2}\\ 1-\frac{3}{8}a^2\mu^2 & 1 & \lambda^2+\alpha^2\dfrac{m-n}{n}-\dfrac{a^2\lambda^2}{8}\left(3\lambda^2+2\alpha^2\dfrac{m-n}{n}\right) & 1\\ \frac{3}{8}b^2\mu^2 & 1 & \frac{1}{8}b^2\lambda^2\left(3\lambda^2+2\alpha^2\dfrac{m-n}{n}\right) & 1 \end{vmatrix}=0. \quad (41)$$

After algebraic reduction, use being made in the secondary terms of the first approximation results (1), (40), &c., we easily deduce from (41)

$$k^2 = \frac{p^2}{\rho} \frac{n(3m-n)}{m} \left\{ 1 - \tfrac{1}{2} p^2 \left(\frac{m-n}{2m} \right)^2 (a^2 + b^2) \right\}, \quad (42)$$

whence

$$k = p(\mathrm{E}/\rho)^{\frac{1}{2}} \left\{ 1 - \tfrac{1}{2} p^2 \eta^2 \frac{a^2 + b^2}{2} \right\}. \quad . \quad . \quad . \quad (43)$$

In a hollow circular section the radius of gyration round the perpendicular to the plane through the centre is given by

$$\kappa^2 = (a^2 + b^2)/2,$$

so that (43) is in agreement with (3) and (22).

The fact that (43) is merely a special case of (3) or (22) may seem to indicate that our separate treatment of the hollow cylinder, or tube, is quite unnecessary. I can only say that having regard to the methods by which (3) and (22) were arrived at—more especially to the fact that in establishing (6) I was dealing with solid cylinders—I had long felt the desirability of an independent investigation.

§ 14. The complete determination of the constants A, A′, C, C′, and of the several displacements, strains, and stresses to the degree of accuracy assumed in (43), though not a very arduous labour, would require more time than seems warranted by the physical interest of the problem. I thus confine my further remarks to the form of the longitudinal displacement w. Substituting their approximate values for the J's and Y's from (39) in (32), we find

$$pw/\mu \cos kt \sin (pz - \epsilon) =$$
$$-\mathrm{A}(1 - \tfrac{1}{4}\mu^2 r^2) - \mathrm{A}' \{ (1 - \tfrac{1}{4}\mu^2 r^2) \log \mu r + \tfrac{1}{4}\mu^2 r^2 \}$$
$$+ \frac{\mathrm{C}p^2}{\mu \alpha^2} (1 - \tfrac{1}{4}\lambda^2 r^2) + \frac{\mathrm{C}' p^2}{\mu \alpha^2} \{ (1 - \tfrac{1}{4}\lambda^2 r^2) \log \lambda r + \tfrac{1}{4}\lambda^2 r^2 \}. \quad (44)$$

Now, considering only their principal terms, it is easily seen that A′/A and C′/C are both of the order $(p^2 ab)^2$. Thus, to the present degree of approximation, we may leave the A′ and C′ terms in w out of account. Also confining ourselves to principal terms, we easily find

$$\frac{-\mathrm{A}}{2(m-n)} = \frac{\mathrm{C}p^2/\mu\alpha^2}{m+n}.$$

Hence, employing the two last of equations (40), we deduce

$$\tfrac{1}{4}\{\mathrm{A}\mu^2-(\mathrm{C}p^2/\mu\alpha^2)\lambda^2\}\div\{-\mathrm{A}+\mathrm{C}p^2/\mu\alpha^2\}$$
$$=-\frac{m-n}{4m}p^2=-\tfrac{1}{2}\eta p^2.$$

We thus have from (44), to the degree of approximation reached in (43),

$$w=w_0\cos kt\sin(pz-\epsilon)(1-\tfrac{1}{2}\eta p^2r^2), \quad . \quad . \quad . \quad (45)$$

where w_0 is a constant which depends on the amplitude of the vibration.

The expression (45) for w is exactly the same as I found in my earlier papers for solid cylinders; the r^2 term representing one of the additions I deem it necessary to make to Lord Rayleigh's assumed type of vibration.

The paraboloidal form of cross section, met with except at nodes or when $\cos kt$ vanishes, seems to me an interesting feature of the longitudinal type of vibrations. Possibly, observations on light reflected from a polished terminal face might lead a skilled experimentalist to interesting conclusions as to the value of η.

It should, however, be borne in mind that, inasmuch as the terminal condition $\widehat{zr}=0$ is not exactly satisfied by the above solution in fixed-free vibrations, there may be a slight departure from the theoretical form in the immediate neighbourhood of a free end.

§ 15. The result (43) is true irrespective of the relative magnitudes of b and a. If b/a be very small, the correctional term is the same as for a solid cylinder of the same external radius. If, on the other hand, b/a be very nearly unity, or the cylinder take the form of a thin-walled tube, we have

$$k=p(\mathrm{E}/\rho)^{\frac{1}{2}}(1-\tfrac{1}{2}p^2\eta^2a^2). \quad . \quad . \quad . \quad . \quad (46)$$

The correctional term is here twice as great as in a solid cylinder of radius a.

§ 16. An experimental investigation into the influence of the shape and dimensions of the cross-section on the frequency of longitudinal vibrations is certainly desirable. In comparing the results of such an investigation with the theoretical results here determined, several considerations must, however, be borne in mind.

Statical and dynamical elastic moduli are to some exten different, so that the value of E occurring in (2) or (3) is not that directly measured by statical experiments[*]. In other words the difference between the observed frequency of the fundamental vibration in a fixed-free bar, and the frequency calculated from the ordinary formula

$$k/2\pi = (1/4l)\sqrt{\mathrm{E}/\rho},$$

if E be determined directly by statical experiments, is not to be wholly attributed to the defect of the ordinary first approximation formula. Again, it must be remembered that E varies[†], often to a very considerable extent, in material nominally the same; so that the difference of pitch observed in different rods cannot without further investigation be safely ascribed to differences in the area or shape of their cross-sections. Further, elastic moduli may alter under mechanical treatment, so that it would be unsafe to assume if a hollow bar were further hollowed or were altered in shape, that its Young's modulus would remain unaffected.

If it were possible to measure with sufficient accuracy the frequency of the fundamental note and several of its "harmonics" in a single rod, one would have a more certain basis of comparison with the theoretical results. Even in this case, however, there is the consideration that in practice the rod must be supported in some way, and this is likely to introduce some constraint not accurately represented by the theoretical conditions. Again, reaction between the vibrating rod and the surrounding medium may not be absolutely without influence on the pitch[‡].

I mention these difficulties because their recognition may prevent a considerable waste of time on the part of anyone engaged in experiments on the subject.

Though somewhat of a side issue, it may be worth remarking that the correction factor $1-\frac{1}{2}p^2\eta^2\kappa^2$ for the frequency in isotropic material contains no elastic constant except Poisson's ratio. Thus observations made on rods differing only in material might throw some light on the historic question whether η is or is not the same for all isotropic substances.

---

[*] See Lord Kelvin's Encyclopædia article on Elasticity, § 75, or Todhunter and Pearson's 'History,' vol. iii. art. 1751.

[†] For the effects of possible variation in the material throughout the bar, see the Phil. Mag. for Feb. 1886, pp. 81–100.

[‡] *Cf.* Lamb, Memoirs and Proceedings Manchester Phil. Society, vol. xlii. part iii. 1898.

The discussion of equations (6) and of the experimental side of the problem has been largely expanded at the suggestion of the Society's referee.

XXXIII. *On the Thermal Properties of Normal Pentane.* *By* J. Rose-Innes, *M.A., B.Sc., and* Prof. Sydney Young, *D.Sc., F.R.S.*[*]

In the year 1894 an experimental investigation of the relations between the temperatures, pressures, and volumes of Isopentane, through a very wide range of volume, was carried out by one of us, and the results were published in the Proc. Phys. Soc. xiii. pp. 602–657. It was there shown that the relation $p=b\mathrm{T}-a$ at constant volume (where a and b are constants depending on the nature of the substance and on the volume) holds good with at any rate but small error from the largest volume (4000 cub. cms. per gram) to the smallest (1·58 cub. cms. per gram).

In the neighbourhood of the critical volume (4·266 cub. cms.), and at large and very small volumes, the observed deviations were well within the limits of experimental error, but at intermediate volumes they were somewhat greater, and, as they exhibited considerable regularity, it is a question whether they could be attributed entirely to errors of experiment. In any case, the relation may be accepted as a close approximation to the truth.

A quantity of pure normal pentane having been obtained by the fractional distillation of the light distillate from American petroleum, it was decided to carry out a similar investigation with this substance; but, as it had been found that isopentane vapour at the largest volumes behaves practically as a normal gas, it was not considered necessary to make the determinations through so wide a range of volume.

---

[*] Read December 9, 1898.

The method employed for the separation of the normal pentane from petroleum has been fully described in the Trans. Chem. Soc. 1897, lxxi. p. 442 ; and the vapour-pressures, specific volumes as liquid and saturated vapour, and critical constants have been given in the same journal (p. 446).

The data for the isothermals of normal pentane were obtained by precisely the same experimental methods as in the case of isopentane, and reference need, therefore, only be made to the previous paper (*loc. cit.*).

There were four series of determinations ; and particulars as to the mass of pentane, and the data obtained in each series are given below :—

Series.	Mass of Normal Pentane.	Data obtained.
—	gram.	
I.	·10922	Volumes of liquid to critical point ; volumes above critical temperature to 280°.
II.	·02294	Volumes of unsaturated vapour from 140° to critical point ; volumes above critical point to 280°.
III.	·005858	Volumes of vapour at and above 80°.
IV.	·001845	Volumes of vapour at and above 40°.

The correction for the vapour-pressure of mercury was made in the same way as with isopentane : when liquid was present it was assumed that the mercury vapour exerted no pressure ; in Series I., above the critical point, one-fourth of the maximum vapour-pressure of mercury was subtracted; in Series II. one-half ; in Series III. three-fourths ; and in Series IV. the full pressure.

The volumes of a gram of liquid and unsaturated vapour are given in the following tables.

Volumes of a Gram of Liquid and of Unsaturated Vapour.

SERIES 1.

Temp.	Pressure. millim.	Volume. cub. cm.	Temp.	Pressure. millim.	Volume. cub. cm.	Temp.	Pressure. millim.	Volume. cub. cm.
130°.	7023*	2·022	170°.	29270	2·269	200°.	26910	3·329
	8194	2·018	(*cont.*)	31990	2·250	(*cont.*)	27670	3·136
	11430	2·008		35040	2·230		29350	2·944
	15100	1·998		38270	2·211		30820	2·847
	18610	1·989		42170	2·191		33060	2·751
	22630	1·979		46180	2·172		36260	2·655
	26810	1·969		50760	2·154		41090	2·558
	31010	1·959		55660	2·135		46560	2·482
	35560	1·950	180°.	19340	2·580		49980	2·443
	40280	1·940		20110	2·557		51920	2·424
	45520	1·930		20770	2·538		54060	2·405
	50450	1·921		21570	2·519	210°.	28410	6·055
140°.	8507*	2·094		22470	2·500		28790	5·666
	9927	2·089		23420	2·481		29180	5·274
	10580	2·085		24570	2·462		29530	4·883
	13230	2·075		25730	2·443		29920	4·492
	15730	2·066		27200	2·423		30400	4·106
	18280	2·056		28550	2·404		31160	3·716
	21300	2·046		30230	2·384		32660	3·330
	24140	2·036		32060	2·365		34200	3·137
	27300	2·027		33970	2·346		36870	2·945
	30670	2·018		36240	2·327		39010	2·848
	34610	2·008		38630	2·307		41970	2·752
	38340	1·999		41100	2·288		46070	2·656
	42710	1·989		44280	2·269		49360	2·598
	46880	1·979		47430	2·250		51950	2·559
150°.	11380*	2·172		50830	2·231		54940	2·520
	14680	2·153		54400	2·211	220°.	31010	6·056
	18770	2·133	190°.	22490	2·900		31610	5·667
	22830	2·114		22750	2·866		32270	5·275
	27840	2·095		23180	2·827		32920	4·884
	33180	2·075		23690	2·789		33670	4·493
	39100	2·056		24310	2·750		34630	4·107
	45700	2·037		25110	2·712		36030	3·717
	53080	2·018		26100	2·673		38540	3·331
160°.	14060	2·272		27230	2·635		40790	3·138
	14330	2·268		28630	2·596		44510	2·946
	16670	2·249		30340	2·558		47320	2·849
	19250	2·229		32340	2·520		51110	2·752
	22000	2·210		34780	2·481		56010	2·657
	25350	2·191		37650	2·443	230°.	33630	6·058
	29010	2·172		41060	2·404		34420	5·669
	32900	2·153		43110	2·385		35320	5·277
	37460	2·134		45310	2·366		36320	4·885
	42200	2·115		47620	2·346		37460	4·495
	47860	2·095		50200	2·327		38930	4·108
	53780	2·076		52950	2·308		40960	3·718
170°.	16560	2·398	200°.	25720	6·053		42530	3·525
	17520	2·384		25890	5·665		44530	3·331
	19020	2·364		26030	5·273		47610	3·139
	20660	2·345		26100	4·881		49680	3·042
	22520	2·326		26190	4·491		52410	2·946
	24460	2·307		26250	4·105		55850	2·850
	26630	2·288		26400	3·715	240°.	36240	6·059

---

* Pressure below vapour-pressure.

SERIES I. (*continued*).

Temp.	Pressure. millim.	Volume. cub. cm.	Temp.	Pressure. millim.	Volume. cub. cm.	Temp.	Pressure. millim.	Volume. cub. cm.
240°. (*cont.*)	37310	5·670	250°. (*cont.*)	45160	4·497	270°.	43780	6·064
	38430	5·278		47720	4·110		45570	5·675
	39770	4·886		49390	3·915		47600	5·282
	41350	4·496		51370	3·720		49990	4·890
	43310	4·109		53890	3·527		51320	4·695
	46170	3·719	260°.	41260	6·062		52890	4·499
	48150	3·526		42850	5·673		54600	4·306
	50870	3·332		44590	5·281	280°.	46310	6·065
	54160	3·140		46530	4·889		48350	5·676
250°.	38810	6·061		49020	4·498		50620	5·283
	40110	5·672		50420	4·304		51960	5·087
	41510	5·279		52190	4·111		53300	4·891
	43230	4·888		54090	3·916		54930	4·696
							56810	4·500

SERIES II.

Temp.	Pressure. millim.	Volume. cub. cm.	Temp.	Pressure. millim.	Volume. cub. cm.	Temp.	Pressure. millim.	Volume. cub. cm.
140°.	8866	30·61	200°. (*cont.*)	18460	14·93	240°. (*cont.*)	14570	25·13
	9055	29·70		19160	14·01		15530	23·27
	9255	28·77		19880	13·10		16600	21·41
	9466	27·85		20660	12·18		17810	19·56
	9682	26·93		21470	11·27		19220	17·71
	9886	26·00		22300	10·35		20380	16·32
160°.	9822	29·71		23130	9·44		21730	14·95
	10570	26·94		23950	8·52		22710	14·03
	11100	25·08		24720	7·61		23750	13·11
	11700	23·22		25330	6·69		24910	12·19
	12340	21·36		25620	6·23		26160	11·28
	13040	19·52	220°.	11960	29·76		27560	10·36
	13420	18·60		12930	26·98		29070	9·45
	13790	17·67		13720	25·11		30700	8·53
180°.	10550	29·73		14580	23·25		32570	7·61
	11380	26·96		15560	21·39		34670	6·70
	12000	25·09		16660	19·55		35790	6·24
	12690	23·23		17900	17·70		36990	5·78
	13450	21·37		18950	16·31		38330	5·32
	14280	19·53		20100	14·94		39830	4·87
	15200	17·68		20950	14·02		41730	4·41
	15700	16·76		21850	13·10	260°.	13340	29·79
	16220	15·84		22810	12·19		14500	27·01
	16770	14·93		23850	11·27		15410	25·14
	17320	14·01		24950	10·35		16440	23·28
	17890	13·09		26140	9·44		17610	21·42
	18460	12·17		27380	8·52		18940	19·57
	19010	11·26		28720	7·61		20480	17·72
200°.	11260	29·75		30080	6·69		21810	16·33
	12160	26·97		30720	6·23		23300	14·95
	12870	25·10		31440	5·78		24410	14·04
	13640	23·24		32160	5·32		25620	13·12
	14510	21·38		32990	4·86		26960	12·20
	15470	19·54		33900	4·40		28460	11·28
	16570	17·69	240°.	12650	29·77		30090	10·36
	17480	16·30		13740	27·00		31900	9·45

SERIES II. (*continued*).

Temp.	Pressure millim.	Volume. cub. cm.	Temp.	Pressure millim.	Volume. cub. cm.	Temp.	Pressure. millim.	Volume. cub. cm.
260°. (*cont.*)	33970	8·53	280°. (*cont.*)	16210	25·15	280°. (*cont.*)	30600	11·29
	36340	7·62		17320	23·29		32550	10·37
	39120	6·70		18580	21·43		34680	9·46
	40630	6·24		20030	19·58		37130	8·54
	42360	5·78		21710	17·73		39980	7·62
	44370	5·32		23160	16·34		43400	6·70
	46640	4·87		24810	14·96		45350	6·24
	49650	4·41		26050	14·05		47680	5·79
280°.	13980	29·80		27410	13·12		50280	5·32
	15230	27·02		28940	12·21		52150	5·05
							54120	4·78

SERIES III.

Temp.	Pressure. millim.	Volume. cub. cm.	Temp.	Pressure. millim.	Volume. cub. cm.	Temp.	Pressure. millim.	Volume. cub. cm.
80°.	2371	116·11	140° (*cont.*)	8325	33·32	200° (*cont.*)	13140	24·40
	2441	112·50		9040	29·74		13930	22·62
	2510	108·90		9435	27·95	240°.	3631	116·59
	2586	105·29		9860	26·16		3988	105·72
	2666	101·64	160°.	3015	116·35		4276	98·40
	2708	99·83		3301	105·50		4603	91·10
100°.	2537	116·17		3532	98·20		4980	83·83
	2770	105·34		3795	90·91		5428	76·61
	2955	98·05		4092	83·65		5958	69·34
	3166	90·77		4448	76·45		6426	63·91
	3405	83·52		4859	69·20		6970	58·54
	3681	76·33		5231	63·78		7372	54·95
	4006	69·09		5652	58·42		7823	51·34
	4190	65·50		5979	54·83		8362	47·75
	4398	61·90		6324	51·23		8965	44·16
120°.	2701	116·23		6733	47·65		9677	40·57
	2951	105·39		7192	44·07		10500	37·00
	3152	98·10		7685	40·49		11480	33·41
	3376	90·82		8284	36·92		12650	29·82
	3638	83·56		8977	33·34		13330	28·02
	3940	76·37		9795	29·76		14090	26·23
	4294	69·13		10260	27·97		14920	24·42
	4607	63·71		10770	26·17		15870	22·64
	4960	58·36		11310	24·37	280°.	3933	116·71
	5234	54·78		11890	22·59		4337	105·83
	5531	51·18	200°.	3317	116·47		4656	98·50
	5859	47·60		3642	105·61		5022	91·19
	6233	44·02		3896	98·30		5440	83·92
	6639	40·44		4190	91·01		5936	76·68
140°.	2861	116·29		4533	83·74		6511	69·41
	3129	105·45		4927	76·53		7024	63·98
	3342	98·15		5401	69·27		7634	58·60
	3587	90·87		5812	63·85		8074	55·00
	3870	83·60		6299	58·48		8596	51·39
	4197	76·41		6665	54·89		9187	47·80
	4577	69·16		7084	51·29		9878	44·20
	4920	63·75		7554	47·70		10670	40·61
	5316	58·39		8066	44·12		11600	37·04
	5607	54·80		8678	40·53		12700	33·44
	5943	51·21		9387	36·96		14050	29·85
	6309	47·63		10240	33·37		14830	28·05
	6717	44·05		11240	29·79		15690	26·25
	7179	40·47		11810	27·99		16680	24·45
	7708	36·90		12440	26·20		17800	22·66

SERIES IV.

Temp.	Pressure. millim.	Volume. cub. cm.	Temp.	Pressure. millim.	Volume. cub cm.	Temp.	Pressure. millim.	Volume. cub. cm.
40°.	858	299·3	120°.	928	357·6	200° (*cont.*)	2415	162·8
	869	293·5		989	334·6		2588	151·5
60°.	857	322·6		1061	311·5		2788	140·1
	889	311·0		1143	288·4		3024	128·7
	956	287·9		1237	265·3		3302	117·4
	1034	264·9		1350	242·5		3458	111·6
	1125	242·1		1485	219·5		3632	106·0
	1236	219·1		1604	202·3		3830	100·2
	1299	207·7		1745	185·3		4049	94·6
	1370	196·3		1854	173·9	240°.	1217	358·7
	1447	185 0		1977	162·5		1299	335·7
	1534	173·7		2116	151·1		1394	312·4
	1580	168 0		2276	139·8		1502	289·3
80°.	882	334·3		2463	128·4		1631	266·1
	946	311·2		2680	117·1		1782	243·2
	1019	288·1		2807	111·4		1964	220·2
	1102	265·0.		2946	105·7		2126	202·9
	1200	242·2		3096	100·0		2318	185·9
	1319	219·3		3264	94·4		2464	174·5
	1424	202·1	160°.	1025	357·9		2629	163·0
	1548	185·1		1093	335 0		2821	151·6
	1642	173·7		1175	311·8		3042	140·2
	1748	162·3		1264	288·7		3301	128 8
	1868	151·0		1371	265·6		3609	117·5
	2006	139·6		1497	242·7		3783	111·7
	2167	128·3		1647	219·7		3975	106·1
	2356	117·0		1783	202·5		4191	100·3
	2463	111·3		1939	185·5		4430	94·7
	2579	105·6		2061	174·1	280°.	1314	359·0
	2705	100·0		2198	162·7		1404	336 0
100°.	892	351·7		2357	151·3		1507	312·8
	936	334·5		2535	139·9		1626	289·5
	1002	311·3		2747	128 5		1765	266·4
	1081	288·2		2996	117·2		1928	243·5
	1171	265·2		3140	111·5		2124	220·4
	1275	242 3		3295	105·9		2301	203·1
	1402	219·4		3468	100·1		2509	186·0
	1516	202 2		3664	94·5		2670	174·6
	1647	185·2	200°.	1121	358·3		2850	163·2
	1749	173·8		1195	335·3		3056	151·8
	1862	162·4		1283	312·1		3296	140·4
	1993	151·1		1382	289·0		3578	128·9
	2141	139·7		1501	265·9		3917	117·6
	2316	128·4		1639	243·0		4104	111·9
	2519	117·0		1805	219 9		4321	106·2
	2638	111·3		1953	202·7		4555	100·4
	2763	105·7		2128	185·7		4815	94·8
	2902	100·0		2264	174·3			
	3058	94·3						

Relation of Pressure to Temperature at Constant Volume. Isochors.

For the smaller volumes isobars were first constructed from the isothermals, and the temperatures at definite volumes were read from the isobars. The data from which the isobars were constructed are given below :—

Isobars read from Isothermals.

Temp....	130°.	140°.	150°.	160°.	170°.	180°.	190°.	200°.	210°.	220°.	230°.
Pressure in metres.	Volume in cub. cms.										
12	2·0066	2·0796	2·1692								
16	1·9958	2·0639	2·1464	2·2546							
20	1·9852	2·0500	2·1266	2·2240	2·3526	2·5600					
24	1·9755	2·0372	2·1094	2·1986	2·3115	2·4715	2·7700				
28	1·9661	2·0254	2·0935	2·1767	2·2780	2·4105	2·6145	3·0840			
32	1·9574	2·0144	2·0790	2·1574	2·2496	2·3650	2·5255	2·7915			
36	1·9486	2·0042	2·0656	2·1398	2·2247	2·3285	2·4635	2·6602	2·9910		
40	1·9406	1·9948	2·0532	2·1256	2·2026	2·2965	2·4160	2·5775	2·8100	3·1960	
44	1·9330	1·9861	2·0417	2·1087	2·1830	2·2695	2·3772	2·5135	2·7000	2·9660	
48	1·9257	1·9776	2·0307	2·0946	2·1652	2·2460	2·3438	2·4630	2·6180	2·8290	3·1180
52	1·9186	...	2·0204	2·0816	2·1487	2·2245	2·3150	2·4225	2·5575	2·7330	2·9590
56	...	...	2·0106	2·0691	2·1335	...	...	...	...	2·6570	2·8460

In the following tables the data for the isochors are given ; those for small volumes were read from the isobars, and those for larger volumes from the isotherms.

Isochors read from Isobars.

Volume.	2·0.	2·1.	2·2.	2·3.	2·4.	2·5.	2·6.	2·7.	2·8.	2·9.	3·0.
Pressure in metres.	Temperature.										
12	129·0	142·5									
16	130·7	144·7	155·35	163·45	169·6						
20	132·4	146·8	157·8	166·3	172·85	177·75					
24	134·15	148·8	160·1	169·1	176·0	181·3	185·35	188·4	190·6	192·1	193·1
28	136·0	150·8	162·5	171·85	179·25	185·05	189·45	192·55	195·0	197·25	198·9
32	137·7	152·9	165·0	174·65	182·4	188·65	193·5	197·4	200·15	...	...
36	139·4	154·9	167·2	177·5	185·75	192·05	197·4	201·5	204·95	207·8	210·2
40	141·0	156·8	169·8	180·4	188·85	195·7	201·25	205·85	209·7	212·75	215·6
44	142·9	158·8	172·05	183·05	191·8	199·05	205·1	210·0	214·3	217·9	220·9
48	144·55	160·95	174·65	185·9	195·0	202·6	208·9	214·25	218·8	222·75	226·3
52	146·3	162·95	176·8	188·3	198·0	206·0	212·75	218·3	223·2	227·7	231·5
56	...	164·95	...	...	...	...	...	222·4	227·75	232·4	...

Isochors read from Isothermals.

Volume.	2·9.	3·0.	3·2.	3·4.	3·6.	3·8.	4·0.	4·3.	4·6.	5·0.
Temp.	Pressure.									
190°......	22500									
200......	29920	28720	27330	26760	26500	26360	26290	26200	26150	26090
210......	37770	35950	33600	32260	31480	30960	30580	30140	29800	29410
220......	45800	43210	39960	37930	36600	35660	34960	34120	33450	32720
230......	53940	50810	46430	43730	41820	40420	39400	38150	37140	36000
240......	......	......	53040	49870	47390	45450	44000	42250	40890	39370
250......	......	......	......	......	52830	50470	48630	46400	44620	42720
260......	......	......	......	......	......	......	53240	50550	48290	45940
270......	......	......	......	......	......	......	......	54670	52050	49260
280......	......	......	......	......	......	......	......	......	55800	52500

Isochors read from Isothermals.

Volume.	5·5.	6.	6·5.	7.	8.	9.	10.	12.	14.	16.
Temp.	Pressure.									
180°......	......	......	......	......	......	......	......	18600	17335	16130
190......	......	......	......	......	......	......	......	......	......	......
200......	25980	25760	25450	25140	24400	23540	22630	20840	19150	17690
210......	28940	28460	......	......	......	......	......	......	......	......
220......	31920	31090	30350	29630	28120	26730	25400	23000	20985	19200
230......	34800	33750	......	......	......	......	......	......	......	......
240......	37790	36400	35140	33940	31750	29830	28110	25150	22730	20680
250......	40740	39000	......	......	......	......	......	......	......	......
260......	43590	41510	39770	38140	35300	32870	30790	27260	24460	22140
270......	46400	44040	......	......	......	......	......	......	......	......
280......	49330	46600	44270	42220	38740	35860	33390	29270	26110	23555

Isochors read from Isothermals.

Volume.	18.	20.	22.	26.	30.	35.	40.	50.	60.	70.	80.
Temp.	Pressure.										
100°......	......	......	......	......	......	......	......	......	......	3965	3532
120......	......	......	......	......	......	......	6725	5640	4849	4249	3782
140......	......	......	......	9880	8985	8025	7250	6055	5190	4535	4026
160......	13640	12865	12115	10825	9735	8635	7772	6465	5515	4812	4263
180......	15030	14060	13180	11695	10475	......	......	......	......	......	......
200......	16370	15210	14215	12520	11180	9830	8775	7250	6150	5345	4726
220......	17695	16370	15220	13330	11880	......	......	......	......	......	......
240......	18980	17505	16250	14160	12570	11020	9800	8010	6805	5900	5208
260......	20225	18610	17230	14980	13260	......	......	......	......	......	......
280......	21465	19690	18200	15790	13975	12200	10825	8815	7462	6465	5699

Isochors read from Isothermals.

Volume.	90.	100.	120.	140.	160.	180.	200.	230.	260.	300.	350.
Temp.	Pressure.										
40°......	......	......	......	......	......	......	......	......	......	857	......
60......	......	......	......	......	......	1485	1347	1182	1053	920	......
80......	......	2705	2304	2001	1773	1589	1440	1260	1123	981	......
100......	3187	2907	2464	2137	1889	1693	1532	1340	1193	1040	896
120......	3404	3098	2620	2272	2005	1794	1622	1419	1262	1100	947
140......	3613	3285	......	......	......	......	......	......	......	......	......
160......	3832	3477	2931	2534	2233	1996	1804	1576	1400	1219	1048
200......	4237	3832	3231	2791	2458	2196	1981	1729	1535	1334	1146
240......	4653	4212	3536	3047	2679	2393	2157	1882	1669	1451	1246
280......	5087	4588	3836	3305	2905	2592	2337	2038	1808	1571	1349

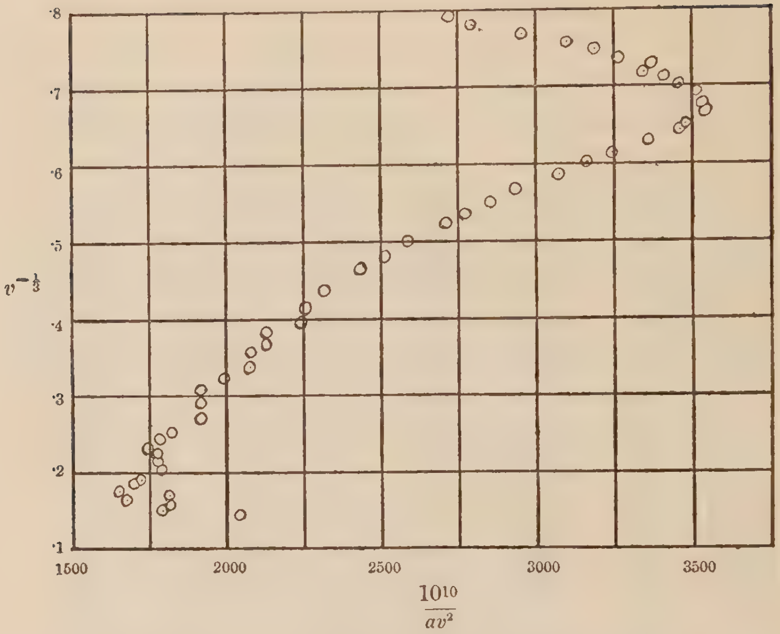
The values of b and a in the equation $p=b\mathrm{T}-a$ were obtained graphically from the preceding data. As with isopentane, the deviations are exceedingly small at the largest and smallest volumes and about the critical volume, but are larger at intermediate volumes; they exhibit a similar regularity and are in the same direction as with isopentane. Here again the relation $p=b\mathrm{T}-a$ at constant volume, if not absolutely true, may be taken as a very close approximation to the truth.

In studying the variation of b and a with the volume it was found convenient, in the case of isopentane, to plot the values of $\frac{10{,}000}{bv}$ and of $\frac{10^{10}}{av^2}$ against $v^{-\frac{1}{3}}$; and this has also been done for normal pentane. The values of b, a, $v^{-\frac{1}{3}}$, $\frac{10^4}{bv}$, and $\frac{10^{10}}{av^2}$ for a series of volumes are given in the table below and, for the sake of comparison, the corresponding values of $\frac{10^4}{bv}$ and $\frac{10^{10}}{av^2}$ for isopentane are added. (Table p. 331.)

The values of $10^{10}/av^2$ are plotted against $v^{-\frac{1}{3}}$ in the diagram on p. 332.

In a former paper by one of the authors (Phil. Mag. xliv. p. 77) it was pointed out that, besides the quantities b and a, it is often useful to consider a fresh quantity τ, which is defined as follows:—For each volume there is one and only one temperature at which the gas has its pressure equal to that given by the laws of a perfect gas; this temperature is denoted by τ. It is also shown that the numerical value

Vol. in c.c.'s.	b.	a.	$v^{-\frac{1}{3}}$.	$10^4/bv$.		$10^{10}/av^2$.	
	From drawn isochors.			N. Pentane.	Iso-pentane.	N. Pentane.	Iso-pentane.
2·0	2312	917,550	·7937	2·163	2·165	2725	2783
2·1	1980	811,210	·7809	2·405	2·487	2795	2952
2·2	1668	698,520	·7689	2·725	2·764	2958	3053
2·3	1436	610,860	·7576	3·028	3·051	3095	3181
2·4	1265	544,000	·7468	3·294	3·365	3191	3329
2·5	1132	490,380	·7368	3·534	3·602	3263	3397
2·6	1010	438,880	·7272	3·808	3·851	3371	3480
2·7	940	409,900	·7181	3·940	4·056	3347	3522
2·8	858	373,910	·7095	4·162	4·279	3411	3586
2·9	790	343,580	·7013	4·365	4·520	3461	3670
3·0	730	316,470	·6931	4·566	4·731	3511	3728
3·2	642·6	276,720	·6786	4·863	4·986	3529	3708
3·4	572·7	244,270	·6650	5·136	5·281	3541	3736
3·6	523·8	221,500	·6526	5·303	5·455	3484	3682
3·8	478·6	200,200	·6408	5·499	5·507	3459	3632
4·0	448·6	186,100	·6300	5·573	5·733	3358	3553
4·3	407·3	166,640	·6150	5·710	5·859	3245	3426
4·6	371·2	149,540	·6013	5·856	5·973	3160	3313
5·0	331·1	130,570	·5848	6·040	6·114	3069	3184
5·5	292·7	112,470	·5665	6·212	6·298	2939	3062
6·0	260·4	97,320	·5503	6·400	6·489	2855	2976
6·5	234·7	85,350	·5358	6·555	6·628	2773	2881
7	212·6	75,210	·5227	6·720	6·786	2713	2816
8	179·5	60,377	·5000	6·964	7·046	2588	2697
9	153·9	49,178	·4805	7·220	7·294	2510	2615
10	134·5	40,923	·4642	7·435	7·541	2444	2564
12	107·5	30,043	·4368	7·752	7·917	2312	2466
14	88·35	22,639	·4149	8·085	8·258	2254	2405
16	74·15	17,388	·3968	8·429	8·463	2247	2327
18	65·15	14,478	·3816	8·524	8·698	2132	2288
20	56·90	11,721	·3684	8·787	8·872	2133	2242
22	51·00	9,938	·3569	8·913	8·979	2079	2172
26	41·50	7,125	·3375	9·268	9·314	2076	2160
30	35·35	5,570	·3218	9·430	9·470	1995	2079
35	29·78	4,261	·3057	9·594	...	1916	...
40	25·47	3,263	·2924	9·815	9·813	1915	1969
50	19·73	2,089	·2714	10·14	10·26	1915	2067
60	16·23	1,521	·2554	10·27	10·46	1826	2046
70	13·75	1,143	·2426	10·39	10·53	1785	1957
80	11·91	894	·2321	10·50	10·49	1748	1788
90	10·45	694	·2231	10·63	10·61	1779	1782
100	9·325	563	·2154	10·72	10·74	1775	1845
120	7·653	388	·2027	10·89	10·87	1790	1823
140	6·520	296	·1926	10·96	10·92	1720	1747
160	5·677	230	·1842	11·01	11·07	1700	1860
180	5·030	187	·1771	11·04	11·18	1650	1930
200	4·478	138	·1710	11·17	11·24	1810	1950
230	3·892	113	·1632	11·15	11·18	1670	1730
260	3·418	81·5	·1567	11·25	11·22	1810	1700
300	2·953	62·0	·1496	11·29	11·27	1790	1680
350	2·513	40·0	·1419	11·37	11·33	2040	1770



of τ is given by the expression $\frac{a}{b-\mathrm{R}/v}$; making use of the values of a and b already given for normal pentane, the values of τ have been calculated, and the results are given in the following Table :—

v.	τ.	v.	τ.	v.	τ.
2·0	488·0	4·6	814·9	35	833·9
2·1	517·1	5·0	824·3	40	841·0
2·2	547·6	5·5	828·8	50	848·0
2·3	576·0	6·0	835·4	60	826·6
2·4	601·0	6·5	838·4	70	810·6
2·5	623·4	7	843·2	80	798·2
2·6	647·4	8	843·3	90	813·6
2·7	660·9	9	848·9	100	817·1
2·8	680·3	10	850·1	120	845·3
2·9	698·0	12	844·9	140	843·3
3·0	715·8	14	849·2	160	821·4
3·2	742·3	16	861·6	180	806·0
3·4	766·5	18	843·2	200	862·5
3·6	780·2	20	854·3	230	824·8
3·8	796·7	22	845·8	260	840·2
4·0	799·7	26	859·5	300	826·7
4·3	807·0	30	849·1	350	869·6

An examination of this table shows that τ remains fairly constant for all large volumes down to about vol. 8. The actual numbers obtained vary a good deal; but these variations are sometimes in one direction and sometimes in another, and there is no steady increase or decrease. It appears, then, that all the values of τ above vol. 8 could be treated as the same without introducing any serious error; this occurred likewise in the case of isopentane. What is still more noteworthy is that the same constant value of τ could be used for both normal pentane and isopentane, keeping within the limits of experimental error. The mean value of τ for all volumes above 8 was found to be 842·4 for isopentane; it is 838·5 for normal pentane; and the intermediate value 840 could be used in both cases without introducing any error greater than the unavoidable errors of experiment.

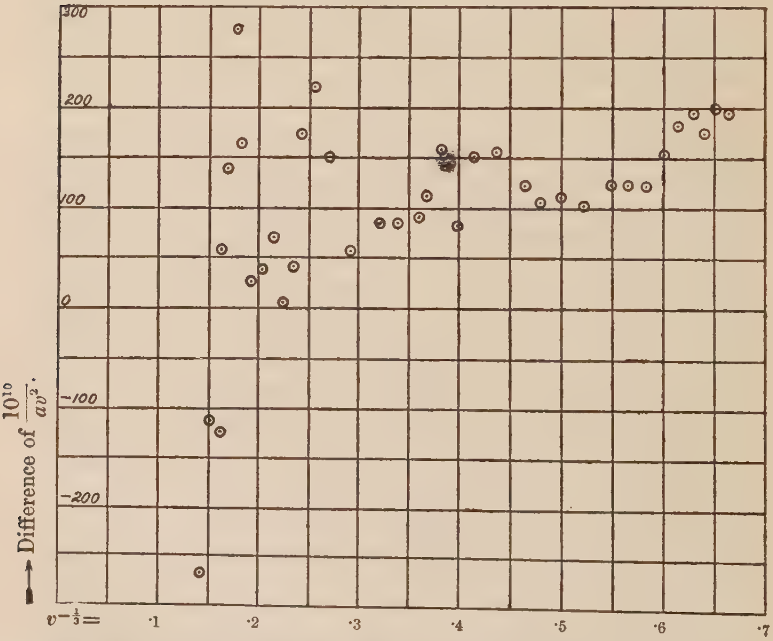
When we pass on to the neighbourhood of the critical point, the value of τ diminishes steadily as the volume decreases. For the critical volume itself τ is about 807, and for vol. 2 it has sunk to 488.

The most important conclusion arrived at in the case of isopentane was that the molecular pressure a does not follow a continuous law, but passes abruptly from one law to another somewhere about vol. 3·4 (Phil. Mag. xliv. p. 79). This inference was based on the study of a diagram in which the quantity $\frac{1}{av^2}$ was plotted against $v^{-\frac{1}{3}}$, and there appeared to be considerable evidence of discontinuity in the neighbourhood of the volume already mentioned. Of course it is impossible to *prove* discontinuity of slope by means of a series of isolated points, but it is suggested very strongly; and even if there be not discontinuity in the true mathematical sense of the term, there seems to be such a rapid change of behaviour as to amount practically to the same thing.

It was therefore a matter of some interest to discover whether the diagram obtained by plotting $\frac{1}{av^2}$ against $v^{-\frac{1}{3}}$ in the case of normal pentane would exhibit the same peculiarity. The diagram is given on p. 332, and it is easily seen that we have here a similar suggestion of discontinuity in the slope of $\frac{1}{av^2}$; this occurs somewhere about vol. 3·4, as with isopentane.

In attempting to find a formula for the pressure of normal pentane we are therefore confronted with the possibility that we may require two distinct algebraic equations. We may simplify the problem considerably by confining our attention to volumes lying above 3·4; and this limitation still leaves us with all those conditions of the substance in which we can most usefully compare it with isopentane.

Looking at the table on p. 331, which gives the series of values of $\frac{1}{av^2}$, and comparing it with the similar table for isopentane (Proc. Phys. Soc. xiii. pp. 654, 655), we notice that at the same volume the value of $\frac{1}{av^2}$ is always smaller in the former case than in the latter. The difference is not great, but it remains too persistently with the same sign for us to disregard it. As we proceed to larger and larger volumes,



however, the difference diminishes on the whole, and an interesting question arises whether we should be justified in treating it as ultimately vanishing when v is made infinite.

To elucidate this point a diagram was drawn in which the differences of $\frac{1}{av^2}$ between isopentane and normal pentane were plotted against $v^{-\frac{1}{3}}$; this diagram is reproduced, p. 334. The diminution in the differences with increase of volume is well shown in spite of the "wobbling" at large volumes; and a line running through the points might apparently end at zero difference. But though this result might be accepted as consistent with the experimental evidence if there were independent grounds for believing in it, it cannot be considered as the most probable judging solely from the diagram; we should be rather led to believe that even at infinite volumes the value of $\frac{1}{av^2}$ for isopentane remained larger than that for normal pentane.

The above results respecting a and τ are chiefly interesting because they seem capable of throwing some light on the vexed question of the influence exerted by difference of chemical structure on the thermal properties of a substance. Concerning this matter very little is known at present; but it is common knowledge among organic chemists that two substances may have the same chemical composition and show practically the same behaviour whilst in the condition of rare vapour, and yet they may differ considerably as to their thermal properties in the liquid state. The great field of observation in which the substances lie between the conditions of a rare vapour and a common liquid has been left almost entirely unexplored. This gap in our knowledge makes it impossible to say in what precise manner the difference between two isomeric substances originates; whether it arises conjointly with the first deviations from Boyle's law, or whether the difference remains inappreciable even with increasing density until we reach the neighbourhood of the critical point. We may put the problem more precisely as follows:—If we imagine the pressure given by a series of ascending powers of the density, what is the lowest power of the density which has different coefficients for two isomeric substances?

We are now able to answer this question with a fair amount of exactness in the case of the two isomers, normal pentane and isopentane. If, as seems most probable, there is a difference between the $\frac{1}{av^2}$ for normal pentane and the $\frac{1}{av^2}$ for isopentane, even at infinitely large volumes, this shows that the coefficients of the second power of the density in the expansion of p must be different for the two substances. On the other hand, if there is no difference between the $\frac{1}{av^2}$ for normal pentane and the $\frac{1}{av^2}$ for isopentane at infinitely large volumes, then the coefficients of the second power of the density in the expansion for p must be the same, since τ has already been shown to have the same value for the two substances at infinite volumes; and the lowest power of the density which has different coefficients for the two isomers must be the third.

It was thought advisable to test these conclusions by a different method. In a former paper by one of the authors (Phil. Mag. xliv. p. 80; see also Phil. Mag. xlv. p. 105) it was shown that in the case of isopentane we might reproduce the original observations very closely by putting

$$p=\frac{\mathrm{RT}}{v}\left\{1+\frac{e}{v+k-gv^{-2}}\right\}-\frac{l}{v(v+k)},$$

where R, e, k, g, and l are constants. If we assume that this formula holds also for normal pentane, and if it be true that the difference of pressure between normal pentane and isopentane at the same temperature and volume varies ultimately as the third power of the density, then we should be able to reproduce the experimental data for normal pentane by means of the above formula, giving to R, e, and l the values already found for isopentane. We may accordingly take $\mathrm{R}=863{\cdot}56$, $e=7{\cdot}473$, $l=5420800$, and we still have the constants k and g left at our disposal to meet the requirements of the normal pentane data. On examining the observations given in Series I. of this paper we find that we can conveniently put $k=3{\cdot}135$, $g=6{\cdot}695$, and we have to test how far the formula with these constants reproduces the experimental results given in Series II., III., and IV. In order to institute an effective comparison between theory and observation a diagram was made in which pv was plotted against $v^{-\frac{1}{3}}$;

the calculated isothermals were drawn as continuous lines, while the experimental values were put in as dots. An examination of the diagram shows that a fair concordance between calculation and experiment has been secured; but the agreement is not so good as could be wished. Deviations amounting to 1 per cent. are not uncommon, and in places they approach 2 per cent. If we have regard to the differences which often occur in inquiries of this kind between the results of independent observers, we might conclude that the above deviations are unimportant, and that R, *e*, and *l* were really the same for the two pentanes as supposed. But it seems more likely that the deviations are too large to be neglected; hence, the most probable inference is that the *l* for normal pentane is not the same as the *l* for isopentane, thereby confirming our former conclusion.

DISCUSSION.

Dr. LEHFELDT asked whether the authors had observed any other singularity or discontinuity at vol. 3·4. He also asked whether the authors were satisfied with ordinary squared-paper in plotting their curves. It ought to be possible to design a machine for doing the work mechanically to an accuracy of $\frac{1}{50}$ of a millim.

Mr. APPLEYARD said the fractionating apparatus devised by Dr. Young was a great improvement on older forms; it ensured that there should always be sufficient, and yet not too much, liquid at each valve-trap. He hoped that details of the tube, in the latest form, would be included in the paper. In the separation of such a mixture as chloroform and alcohol, the common method by water-extraction was imperfect; it was not desirable always to convert the mixture wholly into chloroform. Ordinary fractionating-tubes yielded an impure distillate in this case. Perhaps the difficulty was inherent for these two liquids. Dr. Young's apparatus would put the question beyond doubt.

Dr. YOUNG, in reply, said that the only objection to curve-tracers was their cost. The curves he had obtained from his experimental results were all isothermals; he did not think isobars would indicate anything such as Dr. Lehfeldt had suggested. With regard to such mixtures as chloroform and alcohol, the chances of separation were difficult to predict. A distinction might however be drawn between liquids partially miscible, and liquids miscible in all proportions. Hexane (b.p. 69° C.) and benzene (b.p. 80° C.) for instance, were both hydrocarbons miscible in all proportions, and it might be thought possible to separate them by a fractionating apparatus; but experiment shows they cannot so be separated. Similarly, alcohol and chloroform are miscible in all proportions, and it rests with experiment to decide whether, on distillation, they behave "normally," or whether, like benzene and hexane, they behave as though they are only partially miscible. If they behave "normally," they *can* be separated by fractional distillation, but if they behave like partially miscible liquids, separation by that means is impossible.

XXXIV. *Repetition of an Experiment on a Magneto-optic Phenomenon discovered by Prof. Righi.* *By* Prof. SILVANUS THOMPSON, *D.Sc., F.R.S.*[*]

[Abstract.]

THE experiment was originally described in *Atti R. Accad. Lincei, Roma*, ser. 5, vii. 1898.

A substance absorptive of light is submitted to a powerful magnetic field between the pole-pieces of an electromagnet; the pole-pieces being drilled so that a beam of light from an arc-lamp can traverse the gap *along* the magnetic lines. A polarizing prism is placed between the arc-lamp and the electromagnet, and after having passed through the magnetizing apparatus the beam thus polarized is examined by an analyzer. The analyzer must be turned to "extinction" before the magnetizing current is turned on. If this is done, brightness is restored at the analyzer as soon as the magnetic field is established. The substance absorbing the light in the gap may be nitric-oxide fumes, or an ordinary spirit-lamp sodium-flame. The second effect to be noticed is that when the emergent beam is examined there is a splitting of the lines. Righi explains this by supposing that when light of frequency n is brought into a magnetic field and passed *along* the lines of the field, it is split up into two sets of circular waves, a right-handed and a left-handed set, one of which sets is accelerated and the other retarded. There are now two frequencies, n_1, n_2, one a little higher and the other a little lower than n. But since the analyzer is adjusted to extinguish n, there is brightness for n_1 and n_2. Normally, nitric oxide absorbs green, and red is observed; but when the magnetic field is set up, blue-green light is seen at the analyzer; for there are now two different kinds of light being absorbed, one of higher and one of lower frequency than the normal, and what is observed is the complementary spectrum. Again, if a tube of sodium is warmed to a point far short of that which would cause it to emit visible rays, and the vapour is placed in the magnet gap, at the moment when the magnetic field is set up the D lines, each doubled as in Zeeman's experiment, become visible in the observing spectroscope, *i. e.*, the emission spectrum is obtained of a substance which is not actually emitting light.

---

[*] Read October 28, 1898.

Discussion.

Mr. Blakesley said that no doubt the analyzer was used at the position of extinction for convenience merely. In other positions the eye would be overwhelmed with light.

XXXV. *A Temperature Tell-tale.*

By Rollo Appleyard.

[Abstract.]

This instrument is intended to be used in connection with vats, and for other purposes where an alarm is to be sounded by making electric contact when temperature rises or falls beyond certain limits. A J-shaped glass tube has its short limb sealed and its long limb open. Water or other suitable liquid is poured in, completely filling the short

---

[*] Read January 27, 1899.

limb. Mercury is then made to displace nearly all the water in the short limb; the surplus water in the long limb is removed by a pipette, and the mercury is adjusted to a convenient level. Two platinum contact-wires are sealed into the glass at a short distance above the free surface of mercury in the long limb. The tube may be half an inch in diameter, with a long limb of 5 inches and a short limb of 2½ inches. The quantity of mercury in the tube is generally arranged so that, at temperatures below the boiling-point of the contained liquid, the mercury level is lowest in the long limb. In this case, if the temperature is raised to the boiling-point of the contained liquid, the mercury assumes approximately a common level in both limbs, for at the boiling-point of the liquid, under these conditions, the vapour-pressure is equal to the barometric pressure. Hence the liquid and the mercury are not spurted out.

Discussion.

Mr. Whipple said that when working with an ordinary "thermometer"-tube the contacts were inefficient, owing to oxidation. Moreover, the mercury column broke up, and in some cases mercury clung to the contact-wire. He asked if these difficulties occurred in Mr. Appleyard's apparatus.

Mr. Appleyard, in reply, explained that the change of level in the "tell-tale" was a sudden rise of about an inch of mercury, in a tube about half an inch in diameter. This rise was able completely to envelope the contact-wires, surface oxidation could not affect the working, and there could be no such thing as failure of contact. Moreover, the tube was too wide for mercury to be held up by capillarity. The large area of contact enabled the instrument to be used for strong currents. The cost was small, and the only adjustment consisted in choosing a liquid of suitable boiling-point; for the platinum wires could be sealed in anywhere in the long limb—about 2½ inches from the bottom was a good position for them. The sudden rise occurred when the temperature was one or two degrees above the boiling-point of the contained liquid.

XXXVI. *The Volume-changes which accompany Solution.*

By T. H. LITTLEWOOD, *M.A.*[*]

[Abstract.]

THE apparatus for measuring the contraction observed when solids are dissolved in a liquid consists of two glass bulbs arranged one above the other, so that liquid can pass from the upper one to the lower one through a stopcock, and from the lower one upwards into the neck of the upper one through a second stopcock. This neck, which forms the top of the upper bulb, is fitted with an indiarubber stopper. The lower bulb is tubulured and provided with a glass stopper. A horizontal capillary-tube is fitted into the indiarubber stopper, so that volume-changes can be determined, after the manner of that used in Bunsen's calorimeter. The weighed solid is introduced at the tubulure. The measured amount of water is poured in at the neck. Paraffin oil is now poured in at the tubulure, so that the apparatus is completely filled—the lower bulb with the solid and the oil, the upper bulb with the water. The apparatus is then exhausted, and finally it is placed in a tank of water at constant temperature. When the stopcock between the bulbs is opened, solution begins, and the resulting contraction is measured. For small amounts of salt dissolved in constant volume of liquid, the contraction is very nearly proportional to the amount of salt. For larger amounts, the contraction is greater in proportion than the added salt. If a strong solution is gradually diluted, then, for equal amounts of water added, the contraction becomes smaller for successive amounts of added water.

The author finds Ostwald's theory of osmotic pressure insufficient to express his results, and proposes to add a term depending on the mutual attractions of the dissolved particles, somewhat after the manner of Van der Waals's theory of gases. This, when worked out, expresses the contraction as a logarithmic function of the volumes, which agrees with the observed results better.

DISCUSSION.

Dr. LEHFELDT thought the indiarubber stopper was a weak point in the apparatus. With regard to the theory of the contraction, Tammann (*Zeitschr. für phys. Chem.*, 1894) had given an expression which was rather more intelligible. Tammann found that the effect could be regarded as equivalent to a change of pressure, and, by attributing this quality to the solution, the characteristic surface becomes the same as that for water. The volume of the solution would thus follow similar changes to those that water undergoes with increasing pressures.

---

[*] Read January 27, 1899.

Prof. EWING said the experiments reminded him of the very first piece of research work he had done in physics, which was twenty-five years ago, on the same problem, with Prof. McGregor. An examination of the electrical properties of solutions of certain salts led to an investigation of their changes of density and volume. In some cases the contraction observed was so great that the volume of the solution was less than the original volume of the water to which the salt had been added. They made some measurements, but the apparatus they had used was very rough compared to that described by Mr. Littlewood.

Mr. WATSON asked whether Mr. Littlewood had made any simultaneous density measurements. There were some solutions for which the contractions and corresponding densities had been worked out; and by examining successive dilutions of strong solutions and the corresponding densities, a check might be made as to the numerical results obtained by Mr. Littlewood's apparatus.

Dr. CHREE suggested that, in place of the logarithmic expression, the experimental results might possibly be better represented by a few terms of a series involving integral powers of the difference of volume, each term being multiplied by a proper constant, and asked whether the author had tried a series of this kind.

Mr. LITTLEWOOD, in reply, said that the indiarubber stopper possessed advantages in regulating the height of the liquid in the capillary tube. It did not introduce sensible error, for it was possible to work with it to a centigram of mercury in the capillary. On the other hand, temperature-changes of one-tenth of a degree involved 1 centigram more or less of mercury in the tube. Bunsen, using an indiarubber stopper, obtained very accurate results in calorimetry.

PUBLICATIONS OF THE PHYSICAL SOCIETY.

THE SCIENTIFIC PAPERS

OF THE LATE

SIR CHARLES WHEATSTONE, F.R.S.

Demy 8vo, cloth. Price 15*s.*; *to Fellows*, 7*s.* 6*d.*

Uniform with the above.

THE SCIENTIFIC PAPERS

OF

JAMES PRESCOTT JOULE, D.C.L., F.R.S.

Vol. I. 4 Plates and Portrait, price £1; to Fellows, 10*s.*

Vol. II. 3 Plates, price 12*s.*; to Fellows, 6*s.*

PHYSICAL MEMOIRS.

PART I.—VON HELMHOLTZ, On the Chemical Relations of Electrical Currents. Pp. 110. *Price* 4*s.*; *to Fellows*, 3*s.*

PART II.—HITTORF, On the Conduction of Electricity in Gases; PULUJ, On Radiant Electrode Matter. Pp. 222. *Price* 7*s.* 6*d.*; *to Fellows*, 5*s.* 8*d.*

PART III.—VAN DER WAALS, On the Continuity of the Liquid and Gaseous States of Matter. Pp. 164. *Price* 6*s.*; *to Fellows*, 4*s.* 6*d.*

PROCEEDINGS.

To Fellows of the Society only, at the following prices:—

Vols. I.–IV. 2 vols., cloth, 25*s.*, unbound 23*s.*
Vols. V. & VI. 1 vol., cloth, 13*s.*, unbound 11*s.*
Vols. VII. & VIII. 1 vol., cloth, 13*s.*, unbound 11*s.*
Vols. IX. & X. 1 vol., cloth, 16*s.*, unbound 14*s.*
Vols. XI. & XII. 1 vol., cloth, 16*s.*, unbound 14*s.*
Vols. XIII. & XIV. 1 vol., cloth, 21*s.*, unbound 19*s.*

These prices do not include carriage.

ABSTRACTS OF PHYSICAL PAPERS FROM FOREIGN SOURCES.

VOLS. I., II., & III., 17*s.* 6*d.* each; to Fellows, 13*s.* 2*d.* each.

Applications for these Vols. must be sent direct to
TAYLOR and FRANCIS, Red Lion Court, Fleet Street, E.C.

Blakesley, T. H. A Table of Hyperbolic Sines and Cosines. 1*s.*; *to Fellows*, 9*d.*

Lehfeldt, R. A. A List of Chief Memoirs on the Physics of Matter. 2*s.* 6*d.*; *to Fellows*, 1*s.*

CONTENTS.

XXX. On the Propagation of Damped Electrical Oscillations along Parallel Wires. By Prof. W. B. Morton, M.A. . . . . *page* 281

XXXI. Properties of Liquid Mixtures.—Part III. Partially Miscible Liquids. By R. A. Lehfeldt, D.Sc. 289

XXXII. Longitudinal Vibrations in Solid and Hollow Cylinders. By C. Chree, Sc.D., LL.D., F.R.S. 304

XXXIII. On the Thermal Properties of Normal Pentane. By J. Rose-Innes, M.A., B.Sc., and Prof. Sydney Young, D.Sc., F.R.S. 322

XXXIV. Repetition of an Experiment on a Magneto-optic Phenomenon discovered by Prof. Righi. By Prof. Silvanus Thompson, D.Sc., F.R.S. (Abstract.) 338

XXXV. A Temperature Tell-tale. By Rollo Appleyard. (Abstract.) 339

XXXVI. The Volume-changes which accompany Solution. By T. H. Littlewood, M.A. (Abstract.) 341